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The Effects of Fly Ash on the Ability to Entrain and Stabilize Air in Concrete

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The Effects of Fly Ash on the Ability to Entrain and Stabilize Air in Concrete

by

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Dedication

To my wife and children - This dissertation and all that I have accomplished has been with your help.

To my parents – Thank you for the constant love and support you have given me.

Acknowledgements

I would like to thank my wife, Jessica, and my children, Ethan and Isabel, for having the patience to allow me to accomplish my dreams of becoming a professor. I would also like to thank Dr. Kevin Folliard for giving me a chance to work with him during my Doctorate and Masters. Neither of these degrees nor my wife's undergraduate degree would have happened without you. I will forever be indebted to you. I would like to thank Dr. Fowler for his council and advice. I would like to thank Dr. Juenger for her assistance and guidance with my work in cement chemistry and for allowing me to monopolize her equipment. A thank you needs to be given to Dr. Ken Hover for agreeing to serve on my committee and for teaching me something new every time we interact. I would also like to thank Dr. Wheat for serving on my committee.

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The Effects of Ash on the Ability to Entrain and Stabilize Air in Concrete

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It is common practice to purposely trap small air-voids in concrete in order to give it frost resistance. A large number of factors have been recognized to impact the ability to entrain and stabilize these microscopic air-voids in concrete. This dissertation investigates a number of these variables. However, the primary focus of this work is on investigating problems entraining and stabilizing air in concrete utilizing fly ash. These investigations include: evaluation of existing and newly created test methods to measure the impact of fly ash on the ability to air-entrain concrete, and the fresh and hardened properties of air-entrained fly ash concrete is investigated. Additional work is presented concerning some of the fundamental physical and chemical properties of air-void shells separated from cement paste and how they change with time.

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Chapter 1: Introduction

1.1 INTRODUCTION

Concrete is the most widely used engineering material (Mehta and Monteiro, 2006). Furthermore, it is the most used manmade material (Lomborg, 2001). It is estimated that 6 billion cubic meters are placed every year (Mehta and Monteiro, 2006). This amounts to approximately 1 cubic meter of concrete placed every year for every living human on the earth.

If concrete is going to be utilized in a location where it is exposed to high amounts of moisture and subjected to freezing temperatures, then the concrete should be air-entrained to make it resistant to freezing and thawing (and salt scaling, if applicable). Furthermore, the air-void system in the hardened paste of the concrete should be made up of small and somewhat uniformly spaced voids. An extensive list of items has been provided by Whiting and Stark (1983) that have been shown to impact the ability to entrain and stabilize air-voids in concrete. The totality of this list suggests that almost every aspect of material selection, mixture proportioning, and concrete construction have the ability to impact air-entrainment. While past research has investigated many of these influencing factors, questions still remain about the underlying causes of air-entrainment problems and methods of preventing such problems. Because of this, it can be very challenging to produce satisfactory air-entrained concrete. A better understanding of these systems and their performance would greatly benefit the concrete industry.

The work presented in this dissertation was funded by the Texas Department of Transportation (TxDOT) Research Project 5207, "Effects of Texas Fly Ash on Air-Entrainment in Concrete." The research project was a joint effort by the University of Texas and Cornell University. This project was undertaken because a large number of construction problems were being encountered with air-entrained concrete. The majority of these problems were initially attributed to the use of fly ash in concrete. Fly ash is a by-product from the coal-fired power plant industry that is widely used in concrete and has shown the ability to improve the material properties of concrete. The variable interactions between fly ash and air-entraiment was attributed to changes in the burning process at coal fired power plants in Texas in order to reduce emissions and comply with new standards.

One method that is commonly used in Texas to reduce emissions is to install a different type of coal combustion burner. This burner allows greater control over the amount of oxygen and burning temperature during the combustion process. As this burning process was changed, so was the resulting fly ash. It is often reported that there are changes in the carbon in the fly ash and this has an impact on the performance of air-entraining agents (AEAs) in concrete; carbon present in the fly ash products tends to preferentially absorb AEAs. It is still unclear what aspects of the carbon or other materials in the fly ash are important in determining the demand of the material for the AEAs.

1.2 RESEARCH OBJECTIVES

The main tasks of this research were to:

- Investigate test methods for assessing fly ash and effects on air entrainment

- Investigate test methods to estimate air-void system using fresh concrete
- Develop guidelines for managing air content when using fly ash
- Develop guidelines for air content tolerances, rejection criteria, and mitigation techniques

Further objectives were to:

- Provide a recommendation of some simple test methods that can be used to predict the impact of a given fly ash on AEA demand
- Investigate the reported discrepancy between fresh and hardened properties in concrete
- Investigate the occurrence of air-void clustering in air-entrained concrete

These tasks constitute a very diverse set of research topics that are not only fundamental to properties encountered in the state of Texas but throughout the world where air-entrained concrete is used.

1.3 OVERVIEW OF DISSERTATION

In this dissertation, work is presented that contributes to a number of the bulleted items above.

- The second chapter reviews several existing test methods that can be utilized to assess the AEA demand of different fly ashes from Texas and compares these tests to the performance of the same ashes in concrete.
- In the third chapter more simple tests are investigated. The focus of this chapter is on an existing and a newly designed mortar test to investigate the AEA demand of fly ash.

- The fourth chapter presents a method to assess the AEA demand of fly ash from a single concrete mixture. The work presented in this chapter serves as a base method against which the other methods of assessing the AEA demand of fly ash in concrete can be compared. This work also explores the impact of different AEAs, water reducer, fly ash volume, and mixing temperature on the performance of fly ash concrete with different AEA demands.
- The fifth chapter describes challenges of using two testing methods aimed at measuring the fresh properties of concrete to predict the air-void system and performance in a rapid freezing and thawing test. The use of a device advertised to assess the air-void system in fresh concrete is investigated and comparisons are made to results from a hardened air-void analysis.
- The sixth chapter presents a new experimental technique that was developed to make visual observations of air-voids in the bleed water of cement pastes. These observations suggest that a shell is present around these voids and that this shell may be relevant to resisting changes in the air-void system of concrete.
- Finally, in chapter seven, the air-void shells are investigated with several different analytical techniques in order to relate some of the physical properties observed to the chemical properties of the shells.
- Appendix A shows an investigation of the sensitivity of different parameters on an automated hardened air-void analysis.
- Appendix B provides the procedure used to prepare samples for the hardened air-void analysis utilized in this research.

- Appendix C presents a master collection of the fly ash investigated in project 5207 and their relevant chemical and physical properties.

The research presented in this dissertation is based on work performed by the author at the University of Texas at Austin. Additional research was also performed at the same University related to clustering of air bubbles around aggregates (Naranjo, 2007) and parallel research was performed at Cornell University, focusing on the characterization of fly ash and its impact on air entrainment. These studies will not be presented here, but the key findings from work done at both universities will ultimately be integrated into the final project report for TxDOT 5207.

Chapter 2: Investigation of Air-Entraining Admixture Dosage in Fly Ash Concrete

Abstract

The amount of air-entraining admixture (AEA) needed to achieve a target air content in fresh concrete can vary significantly with differences in the fly ash used in the concrete. The work presented in this chapter evaluates the ability to predict the AEA dosage on the basis of tests on the fly ash alone. All results were compared with the dosage of AEA required to produce an air content of 6% in fresh concrete. Fly ash was sampled from six separate sources. For four of these sources, samples were obtained both before and after the introduction of "low-NOx burners." Lack of definitive data about the coal itself or the specifics of the burning processes prevents the ability to draw specific conclusions about the impact of low-NOx burners on AEA demand. Nevertheless, the data suggest that modification of the burning process to meet environmental quality standards may affect the fly ash-AEA interaction.

2.1 INTRODUCTION

Fly ash is a waste material from the coal combustion process that is typically sent to a landfill if another use is not identified. Fly ash has proven to be a useful supplementary cementing material (SCM) in concrete. Some of the benefits of fly ash include a reduction of cement, improved workability of fresh concrete, decreased permeability, and increased long term strength. Because of these improvements in material performance and sustainability, fly ash is a common SCM for concrete.

The production of a small and well distributed air-void system in concrete is necessary to resist damage from freezing and thawing cycles. To obtain this void distribution, an air-entraining agent (AEA) is added to the fresh concrete mixture to encourage formation and stabilization of these voids. The volume of air in the fresh

concrete needed to prevent damage varies, but is often specified in the range of about 6% of the concrete volume.

This project was initiated in response to reported increases in AEA dosages of up to 500% in the presence of certain fly ashes, discrepancies of up to 5% between fresh and hardened air contents, and problems with reduced strength concrete due to air void clustering around aggregates (Lukehfur, 2004). It was also reported that these problems were encountered in the state of Texas in greater frequency after the incorporation of low-NOx burners in several coal-burning power plants. Similar observations have been reported in the literature (Freeman et al. 1996; Kulaots 2004; Hill and Folliard 2006). Among the objectives of the research project was an evaluation of the loss-on-ignition (LOI) test (ASTM C 311), and the as yet non-standard foam index test (Dodson, 1990) for predicting the potential for interaction between AEA and a given fly ash. This was done by testing 10 separate fly ashes from 6 separate sources using LOI and the foam index test, and comparing those results to the dose of a conventional AEA required to produce an air content of 6% in fresh concrete. This test series was augmented with a limited number of nitrogen adsorption tests on fly ash to gain insight on the possible effects of surface area of either fly ash particles, contaminants, or both. An exciting but coincidental aspect of the work reported here is that fly ash samples were collected from four of the six sources both before and after modification of the burning process to meet U.S. Environmental Protection Agency (EPA) emission standards (via retrofitting with low-NOx burners). While the results are interesting, a lack of information about the input coal or the burning processes themselves prevents the drawing of firm conclusions about the effect of low-NOx burners

2.2 RESEARCH SIGNIFICANCE

In recent years, concrete producers in Texas have faced difficulties with air-entrainment in concrete containing some fly ashes. Specifically, the AEA demand has increased sharply for certain fly ash sources, especially ASTM C 618 Class F fly ashes.

In some cases, the use of affected fly ashes have been banned due to the daily variability of the ashes produced and the lack of a consistent test method to assess these changes. The work contained in this chapter is in response to this need for improved test methods to measure AEA-fly ash interactions.

2.3 EXPERIMENTAL

2.3.1 Samples

Fly ash samples were collected from six different coal-fired electrical power plants in Texas that produce fly ash commercially used in concrete. These samples are labeled numerically, 1-6. Fly ash samples were obtained from four of these locations (1-4) both before and after the modification of the burning process to reduce NOx emission levels, but without sufficient control of samples it is not possible to associate any changes in ash behavior directly with the burning process alone. These samples have been labeled with an "A" or a "B"; "A" label corresponds to ashes after the modification and the "B" label to the ashes before. Samples 5 and 6 are representative ASTM C 618 Class F and Class C fly ashes from the same region whose burning process was not altered. Please note that fly ash samples 2A and 5 are used for testing throughout the dissertation and are labeled as fly ash 7 and 1, respectively, in all other chapters.

2.3.2 Chemical Properties

A chemical analysis of the fly ashes and ASTM C 618 classification are given in Table 2.1. A graphical comparison is shown in Fig. 2.1 and 2.2. The compositional analysis was done using x-ray fluorescence spectroscopy.

2.3.3 Concrete Mixtures

To develop a baseline for comparison, a series of concrete mixtures was prepared in the laboratory in which the 10 different fly ashes were incorporated using the same mass of ash. The mixture proportions are in Table 2.2. During the mixing process, the amount of AEA used was incrementally increased and the air content monitored via the

ASTM C 138 unit weight method. Frequent mix-specific calibrations between the unit weight method and the ASTM C 231 pressure meter method produced a series of trend lines indicating air content as a function of wood rosin AEA dosage. From these data the dose required to stabilize 6% air in the fresh concrete was interpolated for each mixture. Further details on this mixing process follow.

Initially a 64-L batch of concrete was made in an 85-L drum mixer. All of the material for the mixture was stored in the mixing room for at least 24 hours at 23^{o}C prior to mixing to keep the fresh concrete temperature constant. The mixture, shown in Table 2.2, used a water-to-cementitious materials ratio (w/cm) of 0.45 with 335 kg/m^3 (equivalent to 6 sacks of cement) of total cementitious materials, of which 80% was ordinary portland cement that met the requirements for ASTM C 150 Type I and Type II with a 0.53 alkali content (Na_2Oeq), and 20% was the fly ash to be investigated. Local river gravel and sand were used for the aggregate. Coarse and fine aggregates were brought in from the stock piles and individually mixed. A moisture correction for each was used to adjust the batch weights. The gravel and sand were added to the mixture first, and then 2/3 of the mixing water was added. The mixture was agitated for one minute. Next, the cement, fly ash and the remaining mixing water were added and mixed for three minutes. At this point the mixer was stopped and any material gathering on the sides or back of the mixer was removed. During the final three minute mixing period the mixture was brought to a constant slump (ASTM C 143) of 75 mm +/- 25 mm using a normal water reducer. Due to water demand differences of the fly ash mixtures the dosage of normal water reducer varied between 45 and 85 mL/100 kg of cementitious material. The normal water reducer met the requirements of ASTM C 494 as a Type B and Type D. It is expected that different results would be obtained with the same materials when mixed for different durations, at different mixing speeds, or with different mixing energy per unit volume of mixture. Nevertheless, this method allows useful comparisons for the fly ashes investigated.

2.3.4 LOI

The most common hypothesis to explain the fly ash and AEA interaction is that AEA is adsorbed to the surface of unburned carbon particles in the fly ash. It is also commonly understood that LOI is generally a useful indicator of unburned carbon. ASTM C 618 specifies a maximum LOI value of 6% for fly ash, and Texas DOT specifies a maximum limit of 3% (TxDOT DMS 4610 2006). Such specifications are based on work such as that by Gebler and Kleiger (1983). In this project all ten fly ash sources were tested in accordance with ASTM C 311 standards with the procedure published by Harris et al. (2006). Two samples were measured and averaged for each data point reported.

2.3.5 Foam Index

Given the obvious desirability for a test that directly measures fly ash and AEA interaction, researchers such as Dodson (1990) and others (Gebler and Klieger 1983, Kulaots et al. 2003) have proposed multiple versions of what has been called a foam index test. In the many variations of this test, a mixing container is partially filled with a water-and-fly ash slurry, with or without cement or other admixtures. AEA is incrementally added, followed by vigorous agitation of the container. The amount of AEA required to stabilize a foam layer that just covers the surface of the slurry is reported as the foam index, and is a simple but a useful indicator of slurry-AEA interaction as influenced by the specifics of the container, agitation, and other details of the method. Currently there is no established standard for the foam index test. After investigations were made of several different methods the procedure used in this study was chosen due to ease of use and good repeatability of measurements.

For this testing, 25 mL of distilled water, 5.0 g cement, and 5.0 g fly ash were added to a 120 mL glass vial (O.D. x H: 50 x 95mm). The mixture was shaken for 20 seconds and 0.10 mL was added of a solution of 2.5 vol.% wood rosin AEA and distilled water. The mixture was subsequently shaken for 10 seconds and then allowed to rest for 20 seconds

and the foam produced was inspected for stability. The AEA solution is incrementally added and shaken until a stable foam is formed that completely covers the liquid surface after sitting statically for 20 seconds. At this point the volume of the AEA added was recorded and the value reported as μL of AEA/g fly ash. For this testing, the same cement and AEA were used as was used in the concrete testing.

2.3.6 Nitrogen Gas Adsorption

It has been hypothesized that the ash-AEA interaction is influenced by the surface area of an adsorbent within the ash (Kulaots et al. 2004, Hill et al. 1997). If unburned carbon is the primary adsorbent of the AEA, then the carbon surface area may be more influential than the carbon content by mass. A comprehensive examination of this effect would require identifying the critical adsorbent, measuring both its mass and surface area, and comparing these results with indicators such as AEA dose to stabilize 6% air in fresh concrete or foam index values.

Preliminary work in this project included nitrogen adsorption tests in conjunction with Brunauer, Emmet and Teller (BET) analysis on a subset of the ash samples. All BET isotherms were obtained using a Micrometrics ASAP 2000 automated gas adsorption system. The samples were outgassed at 200 ºC for 24 hours prior to analysis.

2.4 RESULTS

All test results are included in Table 2.1, and displayed graphically in Fig. 2.3. Data in Fig. 2.3 have been normalized relative to the values obtained for fly ash 6. This fly ash was arbitrarily selected as the control sample. Perhaps the clearest and most meaningful findings are: 1.) there is significant variation in AEA demand to produce 6% air in fresh concrete (varying from 24 to 147 ml/100 kg cementitious material) and 2.) there is a lack of correlation between AEA demand and any of the other test results. Relative to source 6, in only 2 of the 10 series does an increase in LOI correspond to an increase in the amount of AEA required to stabilize 6% air in fresh concrete. In only 3 of

the 10 series does an increase in foam index correspond to an increased required dose of AEA in concrete.

2.4.1 LOI

A comparison is made in Fig. 2.4 between the LOI values and the AEA dosages required in concrete to produce 6% air content for the fly ash samples in this study. There appears to be no correlation between the two tests. This suggests that the amount of material removed during the 750^{o}C ignition of the fly ash is not a reliable predictor of AEA demand. These findings are similar to those found by Hill et al. (1997) and conflict with work done by Gebler and Klieger (1983).

2.4.2 Foam Index

As can be seen in Fig. 2.5, this test is able to predict AEA demand when large dosages of AEA are required for fly ash samples but it is not able to distinguish between the fly ash samples that require less AEA (with required dosages less than 60 mL/100 kg of cementitious materials).

2.4.3 Nitrogen Gas Absorption

For a limited number of specimens, the surface area was determined by nitrogen gas absorption. The results can be found in Table 2.1. From the samples investigated it appears that a correlation may exist between the AEA demand in concrete and the surface area per unit mass of fly ash. As the surface area per unit mass increases, the AEA dosage requirement in concrete also increases.

In order to examine the effect of the material removed by the LOI test on the surface area per unit mass, the remaining material from fly ash 2A after the LOI test was analyzed with nitrogen gas adsorption. The result is shown in Table 2.1. It is interesting to note that after the high-temperature ignition, the surface area per unit mass of the fly ash was reduced to a value similar to a fly ash with a low AEA demand in concrete. Furthermore, when foam index testing is done with a fly ash sample that has been ignited,

the amount of AEA required to form a stable foam is also reduced to the amount required for a low surface area fly ash. This finding supports the hypothesis that it is the removal surface area, not mass, in the LOI test that controls AEA demand.

2.4.4 Comparison of Fly Ash

2.4.4.1 Fly Ash 1A and 1B

When inspecting the chemical properties of fly ash 1 before and after the altering of the burning process, one can see that there was a 66% increase in the iron oxide levels and an increase of more than 20% in the sodium oxide levels. These changes are significant enough to suggest that a change in the characteristics of the source coal may have occurred between the sampling periods (in addition to potential changes in the nature of the fly ash imparted by the changed burning process). Foam index values increased 32% and LOI actually decreased 33% after the new burning processes were implemented. AEA dosage increased 40% This change in AEA demand was the largest; however, one should note that the initial sample obtained from this source had the highest AEA demand of any of the other initial samples from the other fly ashes. The change in AEA needed in concrete appears to correlate better with the increase with foam index than with carbon content since the LOI value actually decreased.

2.4.4.2 Fly Ash 2A and 2B

The chemical characteristics of the fly ash from source 2 showed approximately a 20% increase in the iron oxide, calcium oxide, and magnesium oxide contents between the two sampling periods. The foam index increased 500%, suggesting that a significant increase in AEA demand should be expected. However, the LOI results from the two samples were similar. The AEA demand in concrete again correlates best with the foam index; this was the largest change between the sampling periods for any of the sources examined (613% increase).

2.4.4.3 Fly Ash 3A and 3B

The chemical properties for fly ash from source 3 did not change significantly between the sampling periods, likewise there was no significant change in foam index test results. There was actually a 90% decrease in the measured LOI between sampling periods. Surprisingly, the AEA demand of the fly ash in concrete increased by more than 60% between fly ash 3B and 3A. Therefore, there is no correlation between AEA demand and any of the fly ash characteristics tested for this fly ash source.

2.4.4.4 Fly Ash 4A and 4B

The chemical properties, foam index, and AEA demand for source 4 did not change significantly between sampling periods, although there was a significant decrease in measured LOI values.

2.5 CONCLUSIONS

This paper has provided information about the chemical and physical characteristics of fly ashes from various coal-burning power plants. These ashes are commonly used in concrete. Among the problems reported from the field are increases in the required dose of AEA at some time after various power plants installed low NOx burners. A full investigation of such reports would require rigorous comparison of both the input coal and the output ash immediately before and after burner change-over, along with careful monitoring of all other coal-to-ash processing and handling steps, coupled with documentation of specific burner types and burning parameters. Such a comprehensive investigation is beyond the scope of this study. Nevertheless, for four different power plants this study was able to document a change in ash-AEA interaction occurring after low NOx burners were installed and any other unknown changes were made to coal-processing, burning, and ash recovery.

Samples 1-4A were obtained from 4 power plants prior to installation of low NOx burners, while corresponding samples 1-4B were obtained from the same plants after

installation of the burners. No accompanying samples of coal (pre- or post grinding) were obtained, and no data were recorded relative to the type of burner, feed rate, or burning temperature. No data were recorded concerning any other changes or maintenance that may have accompanied the installation of the low NOx burners, or any changes to the ash-recovery processes. But against this background, fly ashes from power plants that have been modified with low-NOx burners generally tend to increase the AEA demand in laboratory testing, and this observation generally agrees with the field reports of increased AEA dosages. But what cannot be said with certainty is that the installation of the low NOx burners, per se, is responsible for these observed changes in the ash. It is clear, however, that for the four plants evaluated, ash-AEA interaction changed significantly over the time period associated with a change in the burning process. It is not known whether similar changes would have been observed over a similar time period for ash recovered from plants where no such process changes were made. Given the unquestioned need to control harmful emissions and at the same time produce fly ash that adds value when used as an integral component of concrete, detailed study of how power plant processes affect ash properties is urgently needed.

With regard to screening tests aimed at evaluating fly ash samples, it was observed that LOI measurements did not correlate strongly with the AEA demand in concrete.. The foam index test used in this study showed a satisfactory correlation to the AEA demand in concrete; however, it was unable to differentiate fly ashes with low AEA demand (less than 60 ml AEA/100 kg cm for 6% air in fresh concrete air tests). More work is necessary to refine this test so that it can better resolve differences in these materials. Lastly, limited work was shown in this study with regard to measurements of surface area of fly ash (using BET nitrogen absorption). The results suggest that surface area is a good indicator of AEA demand, especially for the ashes that have been obtained from power plants after the incorporation of low-NOx burners. Furthermore, surface area measurements taken before and after igniting the ash (using LOI procedure) showed a

significant decrease in surface area measured on the ignited samples compared to the as-received ashes. These ignited ashes were then found to respond better to AEAs in foam index testing, suggesting that the carbon lost (along with other impurities/organics) and its associated surface area contributed to AEA demand. Significant follow-up work to this study has been performed or is in progress, and the findings from these studies, including mechanistic work, will be reported in future publications.

Table 2.1 – Chemical and physical properties of fly ashes

	Fly Ash Number	14	26	7	7	24	5	23	10	27	1	2
	Sample Number	1A	1B	2A	2A ig*	2B	3A	3B	4A	4B	5	6
Chemical Tests	Silicon Dioxide (SiO_2), %	50.98	52.56	52.07		48.48	34.47	34.62	37.16	38.07	56.18	30.76
	Aluminum Oxide (Al_2O_3), %	18.84	19.82	23.65		25.01	20.35	21.16	20.55	20.75	20.37	17.75
	Iron Oxide (Fe_2O_3), %	7.87	4.72	4.55		3.56	5.65	5.69	6.06	5.50	6.77	5.98
	Sum of SiO_2,Al_2O_3,Fe_2O_3,%	77.69	77.10	80.27		77.05	60.47	61.47	63.77	64.32	83.32	54.49
	Calcium Oxide (CaO), %	14.39	14.35	12.76		15.92	26.50	25.35	24.76	23.78	9.95	28.98
	Magnesium Oxide (MgO), %	2.91	3.16	2.02		2.50	4.70	4.62	4.29	4.42	2.55	6.55
	Sulfur Trioxide (SO_3), %	0.95	0.92	0.78		0.72	1.71	1.55	1.23	1.11	0.53	3.64
	Sodium Oxide (Na_2O), %	0.57	0.73	0.31		0.30	1.76	1.74	1.63	1.65	0.47	2.15
	Potassium Oxide (K_2O), %	0.94	1.11	0.80		0.71	0.46	0.47	0.45	0.52	1.08	0.30
	Total Alkalies (as Na_2O), %	1.19	1.46	0.84		0.77	2.06	2.05	1.93	1.99	1.18	2.35
	Classification (ASTM C 618)	F	F	F		F	C	C	C	C	F	C
+Physical Tests	mL AEA/100 kg cm for 6% air in concrete	93	64	147		24	50	32	39	38	31	44
	LOI (ASTM C 311)	0.26	0.39	0.79		0.63	0.11	1.12	0.07	0.13	0.12	0.35
	Foam Index (µLAEA /g fly ash)	3.3	2.5	5	1	1	1	1	1	1	1	1
	Surface Area (m^2/g)			4.02	0.66	0.96					0.89	0.95

*A sample of Fly Ash 2A after the completion of the LOI test.

+A wood rosin AEA was used in all tests presented.

Table 2.2 – Standard concrete mixture proportions

Components	Mass (kg/m^3)
Cement	268
Fly Ash	67
Coarse Aggregate	1098
Fine Aggregate	742
Water	151

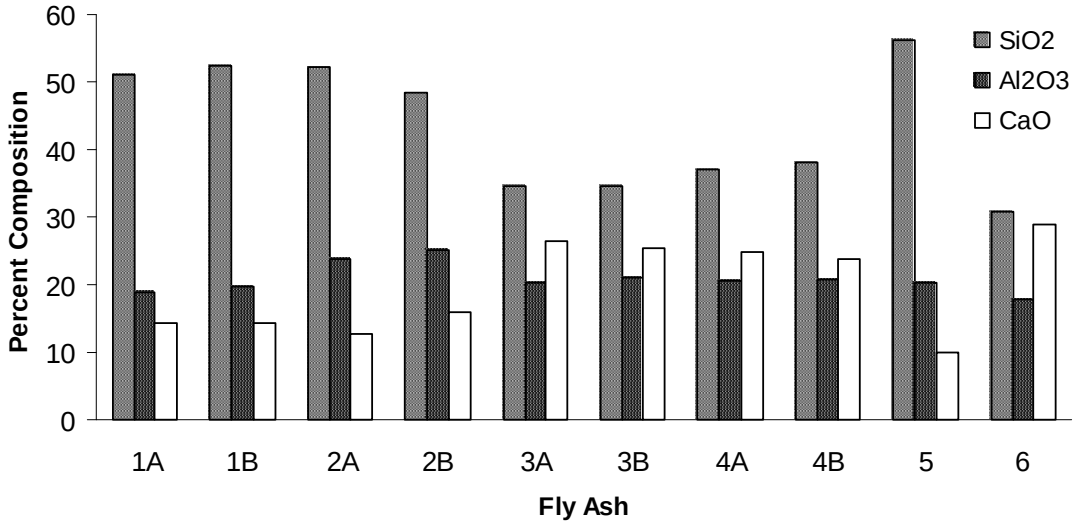


Fig. 2.1 – Fly ash compositions: major components

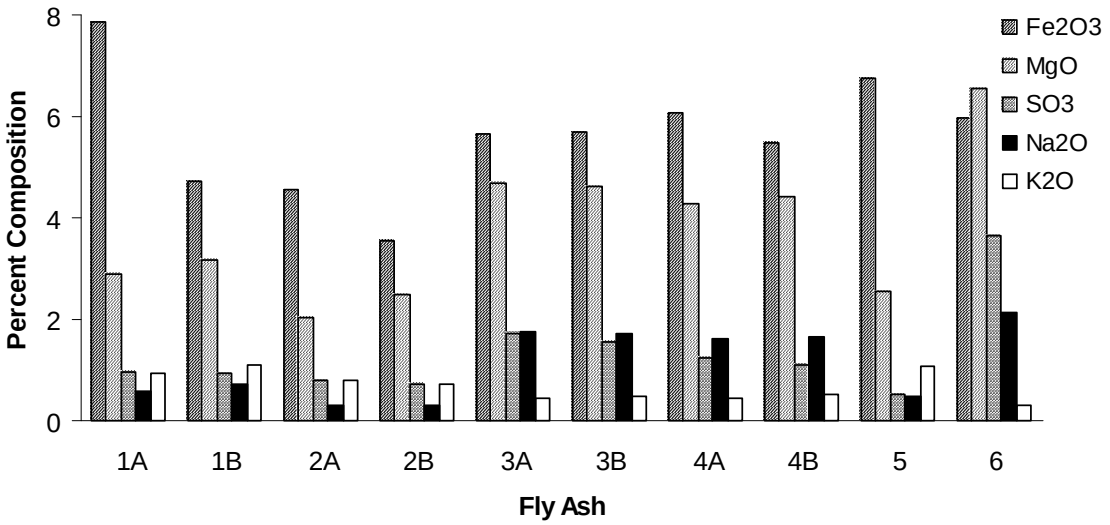


Fig. 2.2 - Fly ash compositions: minor components

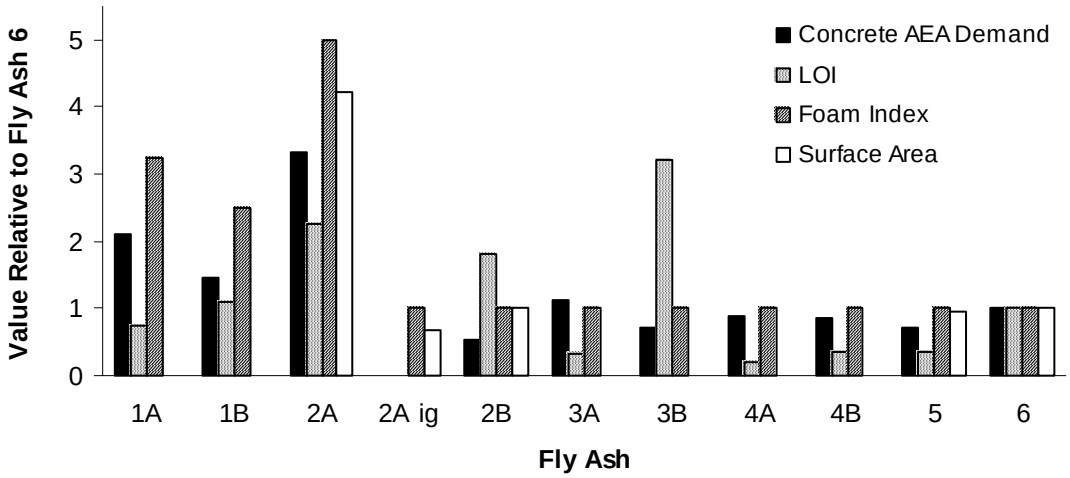


Fig. 2.3 – Physical test results for fly ashes and concrete mixtures normalized to the values for fly ash 6

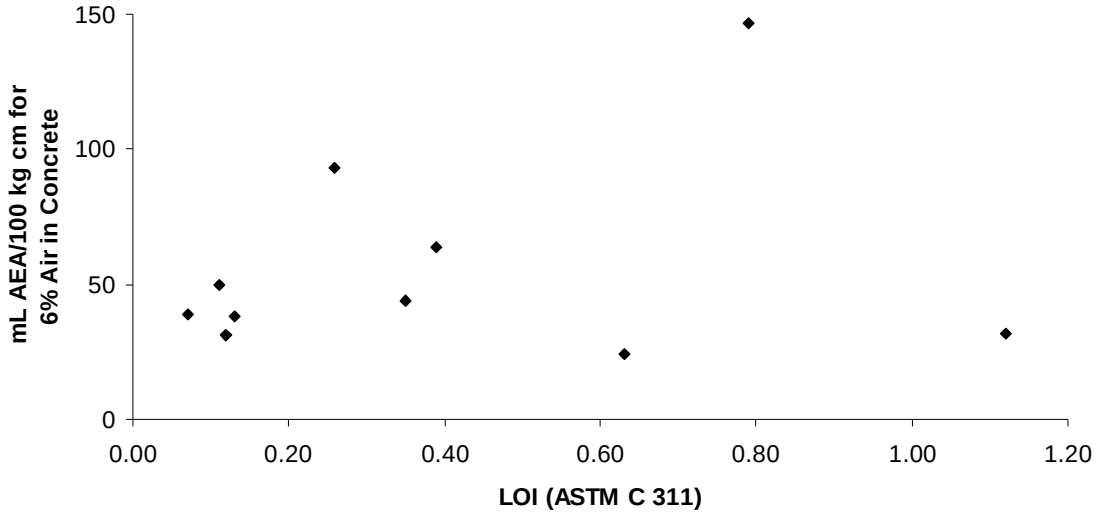


Fig. 2.4 –Dosage of AEA required to achieve 6% air in concrete versus the LOI value of the fly ash.

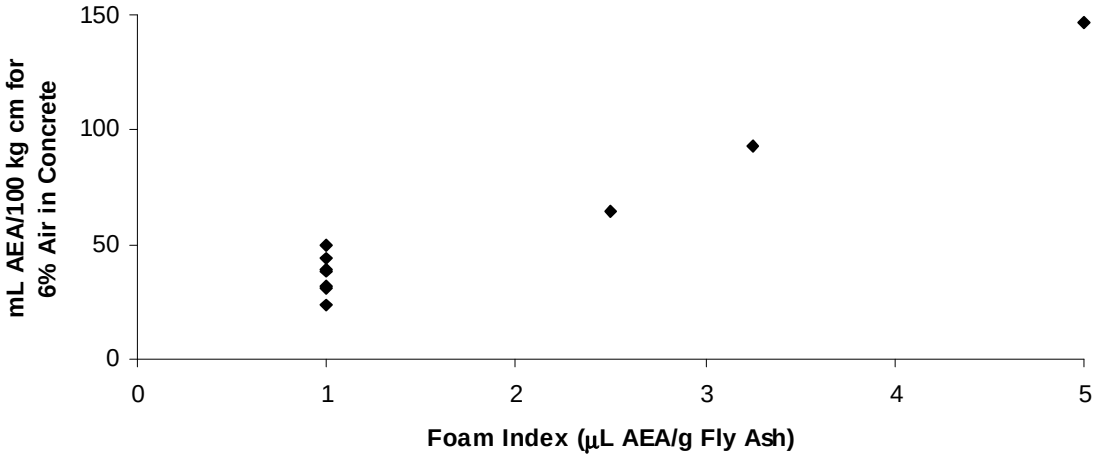


Fig. 2.5 – The results from the foam index test versus the dosage of AEA to achieve 6% air in concrete.

Chapter 3: Evaluation and Improvement of the ASTM C 311 Air-Entrainment of Mortar with Fly Ash Test

Abstract

This chapter examines test methods for assessing air-entrainment in fly ash-containing concrete. A mortar test described in ASTM C 311 "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete" is currently specified by ASTM C 618 "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete" to evaluate the ability to entrain air in fly ash-containing concrete. The work presented here shows the variability of this test to be significant. This variability is attributed to the variable water content and air-entraining agent (AEA) dosage specified in the test. A modified version of the test is developed that has a fixed water content and AEA dosage. The results for this modified test method are evaluated for 15 different fly ashes and an acceptable amount of variability was found. Guidance is given on means to implement this test method with different materials.

3.1 INTRODUCTION

The presence of an adequate air-void system is paramount to the durability of concrete placed in moist environments that undergo freezing and thawing cycles. Although the role of air entrainment in providing frost resistance is undisputed, there are a large number of variables that have been suggested to be detrimental to the formation of an adequate air-void system in concrete. Understanding how various parameters and factors, such as materials, mixture proportions, and construction practice, impact the air-void system is essential in producing frost-resistant concrete.

One of the common problems with the use of fly ash in concrete is that it can impact the dosage of AEA required to produce the desired air content in concrete. Past work has suggested that the amount of residual carbon in the fly ash is the primary cause

of the problem (Gebler and Klieger, 1983). However, work presented in this dissertation (Chapter 2) suggests that the mass of carbon in a fly ash has limited correlation to the ability to entrain air in concrete containing certain fly ashes, and that the mechanism is more complicated.

Tools are needed to accurately evaluate the interactions between concrete mixture ingredients that do not require making a concrete mixture as this is time consuming and costly. Currently, there are only a handful of tools that are designed to evaluate the impact of a fly ash on the ability to entrain air in a mixture. One of these tools is the "Air-Entrainment of Mortar" test described in sections 25 and 26 of ASTM C 311 "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete." This test is currently specified by ASTM C 618 "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete" to evaluate the ability to entrain air in fly ash containing concrete.

3.1.1 Background

3.1.1.1 ASTM C 618 specifications

Certain uniformity requirements are suggested by ASTM C 618 for fly ash used in concrete. One of these requirements is that the dosage of AEA in fly ash concrete should not vary excessively. The current method of evaluating this requirement, according to ASTM C 618, is to limit the loss on ignition (LOI) (ASTM C 311) of a fly ash as to less than 6%, and to determine the amount of Vinsol resin AEA needed to produce 18% air in an ASTM C 311 mortar mixture containing the fly ash in question. It is suggested by ASTM C 618 that the fly ash should not be used in concrete if the required dosage to produce 18% air in the mortar test varies by more then 20% from an established average determined from previous testing results on the material.

3.1.1.2 ASTM C 311 Procedure

In the mortar test presented in ASTM C 311, a standard mixture is prepared with prescribed amounts of cement, fly ash, and standard sand. Proportions for this test are given in Table 3.1. This mixture uses the fly ash to be investigated at a 20% replacement by mass of the portland cement along with an ASTM C 778 standard sand meeting the 20-30 gradation. Water and an AEA are added to produce a flow between 80 and 95 after ten drops on the ASTM C 230 flow table and an air content of 18%. Because it is difficult to produce exactly 18% air content in a mixture, the test suggests that a mixture be produced that contains between 15 and 18% air and another with an air content between 18 and 21%. Then interpolation can be used between the AEA dosages to determine the dosage to produce 18%. The air content of the mixture is determined by the unit weight method with a standard 400 mL measure as specified in ASTM C 185.

In this test the amount of water and AEA needed to meet the flow and the air requirements are unknown and work by Bruere (1956) suggests that these are dependent on one another. Bruere's work suggests that as the water content of a mixture increases so does the air content for mortar mixtures. Due to the test containing two unfixed and interdependent variables, several iterations may be required before a satisfactory combination is found. Furthermore, it may be possible that the difference in water needed to produce a flow at the high and low end of the test method is large enough that it could cause an increase significant increase in the air content. If this were the case then the resulting AEA dosage to produce 18% air content in the mortar mixture and the hence the results of the ASTM C 311 test.

Criticisms of the ASTM C 311 test have been published by Lane (1991). In this work Lane commented that when a mortar mixture is evaluated at 18% air content, the change in the air content for increasing dosage of AEA is small and is therefore not sensitive to changes in the required air content. The work went on to suggest that the dosage of AEA required in the test is significantly higher than what is typically required

in concrete and that because of this higher concentration of AEA the ingredients in the mortar mixture may behave differently then in concrete. . In a broad statement about ASTM mortar based testing, Struble (2006) questioned why the flow of a test could not be measured with a standard water content instead of the water content being determined by the flow in the test.

3.1.2 Objectives

This chapter presents an examination of the reliability of the ASTM C 311 "Air Entrainment of Mortar" test with goal of finding a mortar based test that provides a simple, economical and precise way to evaluate the AEA demand of a fly ash.

3.2 EXPERIMENTAL METHODS

3.2.1 Materials

In this investigation, a portland cement meeting the ASTM C 150 specifications for Type I and II with a 0.53 alkali content (Na_2Oeq) and a Blaine fineness of 3630 cm^2/g was used. The crystalline phases of the cement were determined by a Rietveld analysis and are reported in Table 3.2. Two fly ashes were investigated that are commercially used in concrete and meet the ASTM C 618 classification for a Class F fly ash. The oxide analysis and the dosage of AEA to produce 6% air in concrete for these fly ashes are given in Table 3.3. The two fly ashes were chosen because they represent samples requiring a high and low dosage of AEA in concrete to produce 6% air. At least two mixtures were prepared for each investigation presented in order to ensure reproducibility and the results were averaged.

3.2.2 Evaluation of ASTM C 311

In order to separate the effects of the water content and the AEA dosage in the testing, a constant dosage of AEA was used in the mixture shown in Table 3.1 and then different water contents were tested until the flow was within the acceptable range. At

this point the air content of the mixture was recorded. Mixtures with water contents to produce flows at the high and low limits of the test were investigated to examine how the resulting air content changed.

3.2.3 Modification to ASTM C 311

Modifications to the ASTM C 311 test were investigated. A mortar test is needed that:

- highlights the difference between fly ashes with significantly different AEA demand in concrete
- minimizes the number of mixtures to be investigated to complete a test
- has an acceptable variability
- utilizes a representative water-to-cementitious materials ratio (w/cm) of practical concrete
- is compatible with various commercial AEAs
- utilizes a standard mixing procedure and aggregate

Key variables in the ASTM C 311 test were altered to investigate a new version of the test. These variables were: the method of flow testing, the amount of material, and w/cm.

3.2.4 Comparisons to AEA Demand in Concrete

The ultimate validation of a simplified screening test is to compare the results to the impact on AEA demand of a concrete mixture. To make this comparison, a series of concrete mixtures were prepared in the laboratory with 15 different fly ashes at a 20% replacement of cement by mass, with a 0.45 w/cm and normal water reducer to obtain a slump (ASTM C 143) of 75 mm +/- 25 mm. The mixture proportions are given in Table 3.4.

During mixing the amount of wood rosin AEA in the mixture was incrementally increased and the air content was monitored via the ASTM C 138 unit weight method.

Frequent mix-specific calibrations between the unit weight method and the ASTM C 231 pressure meter produced a series of trend lines indicating air content as a function of AEA dosage. From these data the AEA dose required to stabilize 6% air in the fresh concrete was interpolated for each mixture. Further details on this test procedure can be found in Chapter 4 in this dissertation.

3.3 RESULTS AND DISCUSSION

3.3.1 Evaluation of ASTM C 311

Because the test results are dependant on both the flow and the air content of the mixture it was decided that mixtures would be prepared with a constant dosage of Vinsol resin AEA and then the water content would be varied until the flow was within the renge specified by ASTM C 311. This approach was necessary as it is commonly understood that the workability or flow and air content of a mixture have been shown to be related (Bruere, 1956). After the desired flow was obtained the resulting air content was recorded. This process was continued until a mixture was found with an air content between 15% to 18% and 18% to 21%. At this point interpolation was used between two data points to determine the dosage of AEA required for the mixture to produce 18% air content. Results of the ASTM C 311 testing are shown in Fig. 3.1. This plot shows the air content and AEA dosage along with the corresponding w/cm needed to produce the desired flow for two different fly ashes. A horizontal line is included to highlight the 18% air content required in ASTM C 311. Red lines are also included that correspond to mixtures that are at the high end of the allowable flow with air contents between 18% and 21%. The results of the test are shown with vertical lines and circles show the results of the test. The average percent difference between these two results for fly ash 1 is 48%. A large difference between the results for the Fly Ash 7 was not found. As Lane (1991) suggested because the results of the test are not sensitive at this high air content that differences in water content of the mixtures have an ability to increase the air entrained in

the mortar mixture as suggested by Bruere (1958). Because these results are interpolated to find the amount of Vinsol resin AEA needed to produce 18% air inside concrete this difference in air content can skew the results.

The variability in the test results are larger for fly ash 1 than is allowed between two separate grab samples that are to be compared to itself as specified in ASTM C 618. This large variability brings the usefulness of this test into question. Furthermore, it is time consuming to obtain valid data points as several mixtures are required to determine a mixture with an adequate flow and air content between 15% and 18% and then again for 18% and 21%. This test could be improved if this dependence on flow was removed as it not only appears to be a source of the variance but also requires a large number of mixtures to be prepared to investigate a fly ash.

3.3.2 Modifications to ASTM C 311

At the outset of the modification it was decided that certain parameters should not be changed as they help ensure repeatability in the test. It was decided that the mixing procedure and sand specified in ASTM C 311 should not be changed. From preliminary testing it was determined that the flow specified in the test can lead to wide variations in the water content in the test. Furthermore, the wide variation in the flow in the original test was shown to cause the large variability in the standard test method. Therefore, it was decided that the water content utilized in the test should no longer depend on flow and instead be fixed at 0.42 w/cm and the flow would just be measured as suggested by Struble (2006). It was also decided that the measurement of the flow should be modified to be measured in accordance with ASTM C 1437. The primary difference between the two procedures is that the flow would be measured after 25 drops instead of the 10 required previously. By using a larger number of drops more energy is imparted on the mortar before it is evaluated and the material is able to reach a flow that is near the maximum for the material. The amount of material in the test was increased because

there was concern that the original test did not ensure that enough properly mixed material is available to evaluate the air content and flow of the mortar. The mass of cement and fly ash were increased 5% compared to the original ASTM C 311 mixture.

3.3.2.1 Ratio of cementitious materials to sand

In order to optimize the mixture to highlight the performance in air entrained in the test different ratios of cementitious materials to sand (cm/sand) were investigated as the first step to find a mixture proportion that showed the most significant sensitivity to the amount of AEA in the mixture. In Figs. 3.2 and 3.3, the air content and flow of the mortars with different cm/sand (0.25 to 0.31) were investigated with different dosages of tall oil AEA (0 to 290 ml AEA/100 kg cm). In each of the mixtures fly ash 1 was used and the mixture proportions were adjusted to provide approximately the same mixing volume. In both Figs. 3.2 and 3.3 one can see that the air content increases in the mixture as the AEA dosage increases and as the cm/sand decreases. There was very little change in the percent flow at the different AEA dosages but the flow increased as the cm/sand increased. The flow of the non air-entrained sample was not measurable when the cm/sand is decreased below 0.28.

In designing a test it is beneficial to use a mixture that shows the largest difference between the variables of interest. For this reason a cm/sand of 0.28 was chosen to be investigated further. A line is provided in Fig. 3.2 and 3.3 to highlight the flow and air content at this ratio. The resulting proportions of the mixture are presented in Table 3.1 as the modified mixture.

3.3.2.2 Dosages of AEA

Different dosages of a tall oil AEA were investigated and the air content and flow of the mortar mixture are shown in Figs. 3.4 and 3.5 for fly ash 1 and 7. For both fly ashes the air content and flow start from a low value and increase with increasing AEA dosage to some limiting value. Fly ash 1 starts at an air content of around 14% and

increases with increasing dosages of AEA to a limiting value of around 18% air in the mixture. This seems to be the maximum amount of air that is able to be produced as the values do not drastically change with increased amounts of AEA. The mixture with fly ash 7 starts at an air content of around 10.5%t and builds at a slower rate compared to the other mixtures and ultimately gets to the same limiting air content of around 18%; however, the dosage required to get to this point is much larger. The behavior of the flow follows a similar trend and seems to reach a limiting value of 100.

As shown in Table 3.3 there is a large difference in the AEA required to entrain 6% air in concrete between the two fly ashes and so one would anticipate a large difference in response between the test results of these two materials in a mortar mixture. By testing these two fly ashes an investigation can be made of the most significant difference in behavior in the test to be observed. This point appears to be at a dosage of tall oil AEA of 128 mL AEA/100 kg of cement. This dosage is highlighted with a line on Figs. 3.4 and 3.5. By focusing on the air content and flow produced in a mixture at this dosage of AEA there is the widest difference in performance between these two fly ashes. By preparing mixtures at this fixed dosage of AEA a direct assessment of the AEA demand of a fly ash can be assessed by comparing the air content in the mixture at this fixed dosage of AEA against some established average. While other points of comparison may be possible, especially if different sand contents, mixing methods, or mixture proportions are utilized, this combination was chosen as it satisfies the goals established for the modified test method.

In order to investigate different commercially available AEAs in the modified mortar test, mixtures containing fly ashes 1 and 7 were investigated at AEA dosages of 0, 128 and 512 mL of AEA/100 kg of cement for a tall oil, synthetic, wood rosin, and Vinsol resin AEA. These dosages were chosen as they showed the most promise from the investigations with the tall oil AEA. As can be seen in Fig. 3.6 and 3.7 the air content and flow increased as the AEA dosage increased for all of the AEAs investigated. It was

noticed in the air-entrained mortar mixtures that the air content of the mixtures increase at different rates and each had different maximum values depending on the AEAs used. This performance is as expected as the manufacturer-suggested dosage rates for these AEAs are different and hence their effectiveness to entrain air and reach a certain maximum value are different depending on the product. However, for all of the AEAs investigated there is a measurable difference in the amount of air entrained at a dosage of 128 mL of AEA/100 kg cm. This dosage of AEA will still be able to serve as a useful point of comparison of the AEA demand for different fly ashes. However, if one were to use a different AEA than what was investigated in this study then a different dosage may be needed. Some care should be taken in investigating different AEAs to be sure the dosage rate used in the test provides a meaningful difference in performance between a fly ash with a high and low AEA demand.

3.3.2.3 Variability of Modified ASTM C 311 with a Wood Rosin AEA

Finally, the average percent difference is shown in Table 3.5 for replicate mixtures made with 15 different fly ashes using the modified mixture proportion shown in Table 3.1 with a wood rosin AEA. Low average percent differences are shown for the flow and air content determined by the modified mortar test method. The average percent difference of 2.3% for the air content is much improved over the 48% as determined for ASTM C 311.

3.3.3 Comparison of Modified ASTM C 311 to AEA Demand in Concrete

In Fig. 3.8 the dosage of wood rosin AEA to produce 6% air content in concrete is plotted against the air content produced in the mortar mixture for a 128 mL of AEA/100 kg of cm using the same fly ash and wood rosin AEA in each test for 15 different fly ashes. The correlation shown in the graph shows that as the AEA demand of the fly ash in concrete increases the air content produced in the modified mortar air test decreases for a standard dosage of AEA. There appears to be a general correlation of the performance

of the mortar air test and the impact the fly ash has on the ability to entrain air in concrete.

3.4 IMPLEMENTATION

This modified test method could be used in several ways to evaluate the changes of AEA demand of fly ash to be used in concrete. However, the most probable method is to use this test as a substitute for the ASTM C 311 mortar test. This would allow the air content of a fly ash in question to be determined with a fixed AEA dosage and w/cm to be compared against a historical average established for that material. If changes of the air content determined by the test were larger than two standard deviations or 0.60% then this would provide a greater than 95% confidence interval that the AEA demand of the fly ash has changed. A confidence interval of 95% is widely used in the specifications to establish reasonable limits of the test results.

While materials were chosen in an attempt to bracket the practical combinations of cement, fly ash, and AEA that may be utilized in this test it may be possible that a material combination is investigated that does not give satisfactory results. If this occurs then the same development steps presented should be taken with those materials and the mortar mixture proportions adjusted so that satisfactory results are obtained. This may involve using different cm/sand, water content, or AEA dosages as these have been determined to be the major variables affecting the performance of the test besides the mixing procedure and the sand type and gradation.

3.5 APPLICATIONS OF FINDING TO OTHER ASTM MORTAR TESTS

It is common in ASTM methods that utilize mortar to prescribe a flow in order to standardize the water content in the mixtures investigated. It would be beneficial if other ASTM tests that utilize mortar were evaluated to investigate the variability of the test by investigating the results at the extremes of the allowed flow. One test that should be evaluated is ASTM C 185 as this test is very similar to the ASTM C 311 test but is used

to evaluate the impact of cement on the ability to entrain air in mortar. This test has the same dependence on flow and air content that was shown to cause the large variability in the ASTM C 311 test.

3.6 CONCLUSIONS

This work has shown that the current version of the "Air Entrainment of Mortar" test described in section 25 and 26 of ASTM C 311, "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete" is variable. It appears that because the flow and air content are allowed to vary that the results in the test has been shown to have an average percent difference of 48% between two valid results of the investigated fly ash. While there is no precision and bias statement included in ASTM C 311, ASTM C 618 suggests that the fly ash mortar mixtures investigated in ASTM C 311 should not vary by more than 20% from an established average for the fly ash being investigated. This suggests that changes need to be made to the current test as the variation in the test is capable of being larger then suggested limits for the established average.

Work has been presented in this paper concerning improvements on this ASTM C 311 test. These improvements were made by establishing a standard mortar mixture and AEA dosage that highlighted the difference in performance of two fly ashes known to have high and low AEA demand in concrete. The performance of this test has been evaluated with 4 different commercially available AEAs and 15 different fly ashes. The results of the test have been compared to the wood rosin AEA dosage requirements for concrete mixtures with 15 different fly ashes and satisfactory correspondence was shown. An average percent difference in the modified test of 2.3% and 7% was shown to exist for the air volume and flow measurements respectively. This is an improvement over the 48% shown for the existing method. Furthermore, the modified test reduces the number

of mixtures required to evaluate the performance of a fly ash in a mixture from approximately six to two. Finally, some guidance is given on possible methods to implement the test. This guidance is structured so that this new test method could be substituted in place of the previous methods with minimal changes.

Table 3.1 – Mortar mixture design

	ASTM C 311	Modified Mixture
portland cement	300 g	312.5 g
fly ash	75 g	78 g
standard sand 20-30	1125 g	1395 g
water	A	164 g
AEA	B	0.5 mL*

A - Amount to produce a flow of 80-95 in ten drops on the ASTM C 230 flow table
B - Amount of Vinsol resin to produce an air content of 18%
* - equivalent to 128 mL of AEA/100 kg of cm

Table 3.2 – Composition of the Type I/II cement as determined by RQXRD

phase	percentage
C_3S	68.0
C_2S	15.7
C_3A	2.7
C_4AF	8.7
gypsum	1.3
$CaCO_3$	2.6

Table 3.3 – Oxide analysis, LOI, and AEA demand in concrete with fly ash

Fly Ash	1	7
Silicon Dioxide (SiO_2), %	56.18	52.07
Aluminum Oxide (Al_2O_3), %	20.37	23.65
Iron Oxide (Fe_2O_3), %	6.77	4.55
Sum of SiO_2,Al_2O_3,Fe_2O_3,%	83.32	80.27
Calcium Oxide (CaO), %	9.95	12.76
Magnesium Oxide (MgO), %	2.55	2.02
Sulfur Trioxide (SO_3), %	0.53	0.78
Sodium Oxide (Na_2O), %	0.47	0.31
Potassium Oxide (K_2O), %	1.08	0.80
Total Alkalies (as Na_2O), %	1.18	0.84
Classification (ASTM C 618)	F	F
LOI (ASTM C 311)	0.12	0.79
mL AEA/100 kg cm for 6% air in concrete	32	147

Table 3.4 – Concrete mixture design

Components	Mass (kg/m^3)
Cement	268
Fly Ash	67
Coarse Aggregate	1098
Fine Aggregate	742
Water	151

Table 3.5 – The average percent difference for the percent air content and flow of replicate mixes of 15 different fly ashes with a wood rosin AEA with the modified mixture.

	average % difference	
	air content	flow
average	2.3	7
maximum	5.4	16
minimum	0.5	0

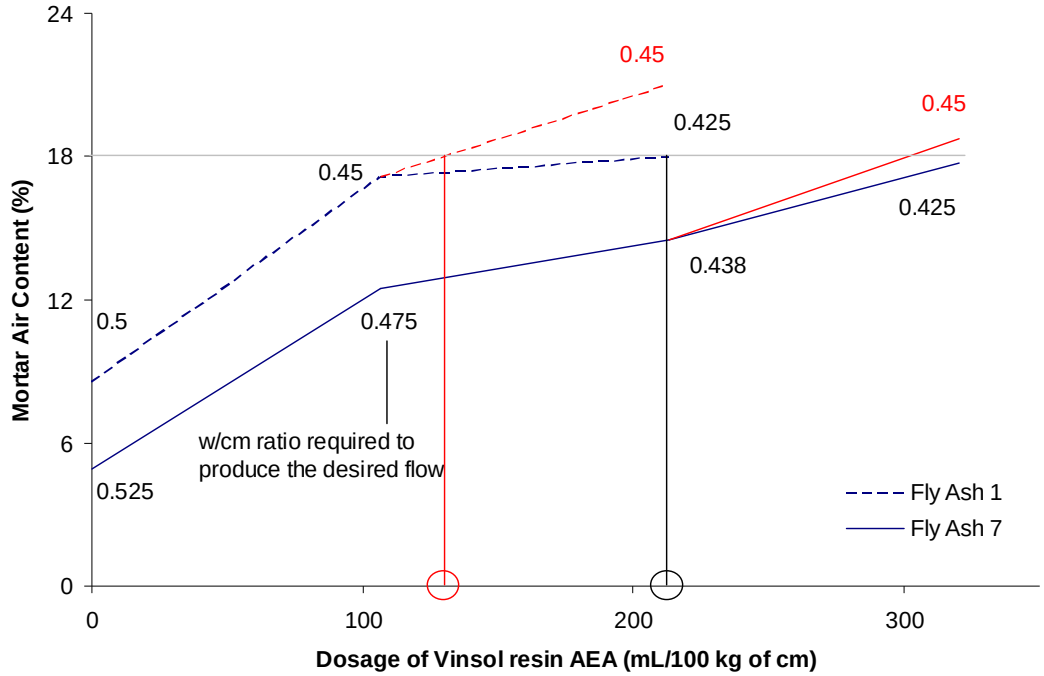


Fig. 3.1 – ASTM C 311 results with fly ash 1 and 7

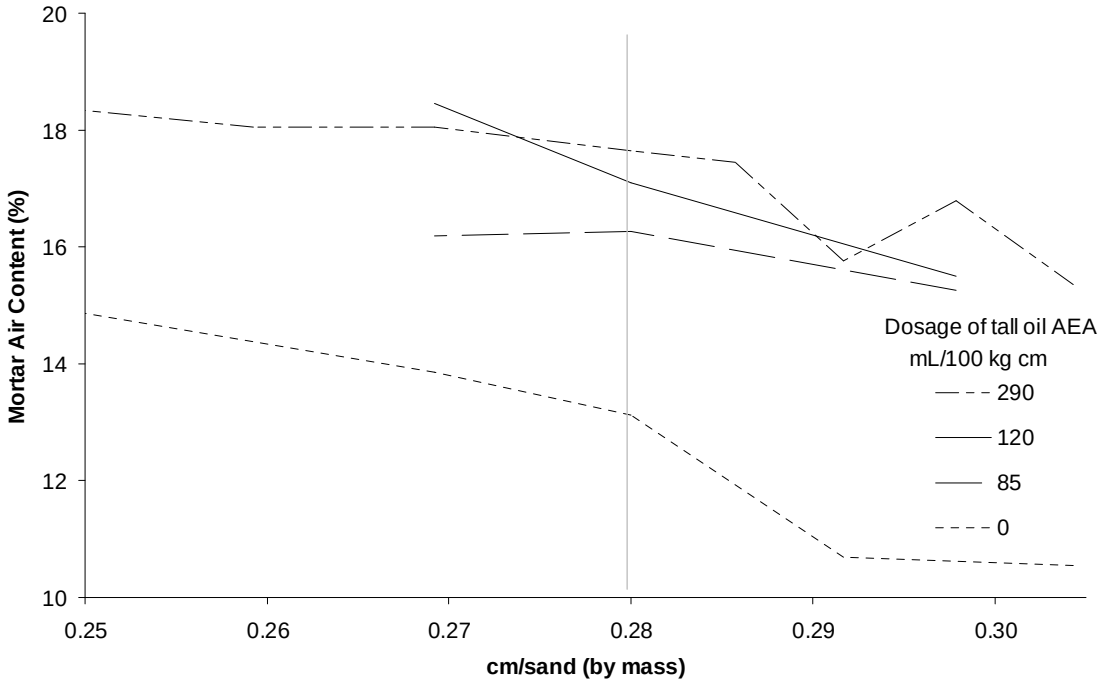


Fig. 3.2 – The change in air content for different cm/sand and different dosages of tall oil AEA with fly ash 1.

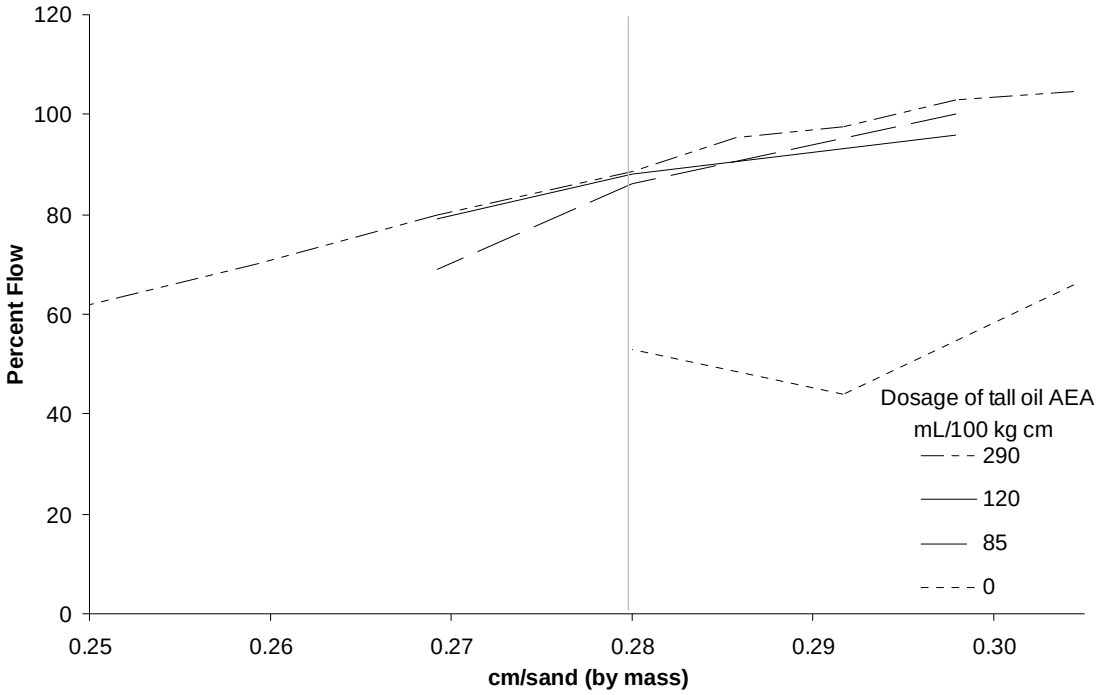


Fig. 3.3 – The change in flow for different cm/sand and different dosages of tall oil AEA with fly ash 1.

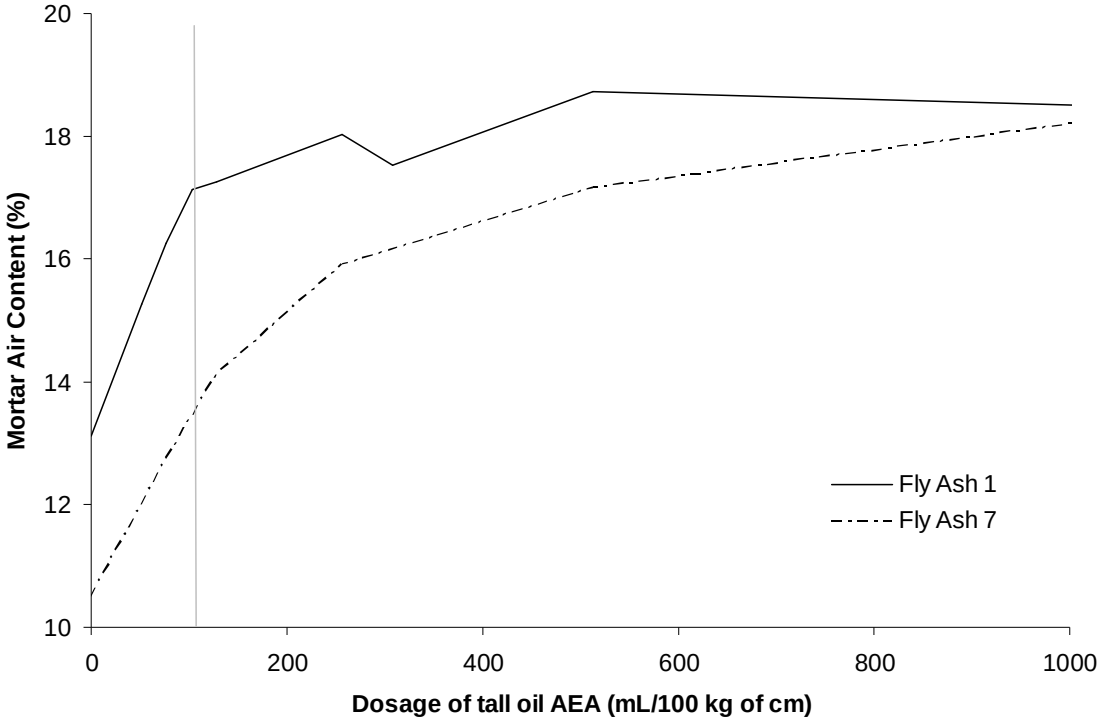


Fig. 3.4 – Air content of a modified mortar mixture with various dosages of tall oil AEA.

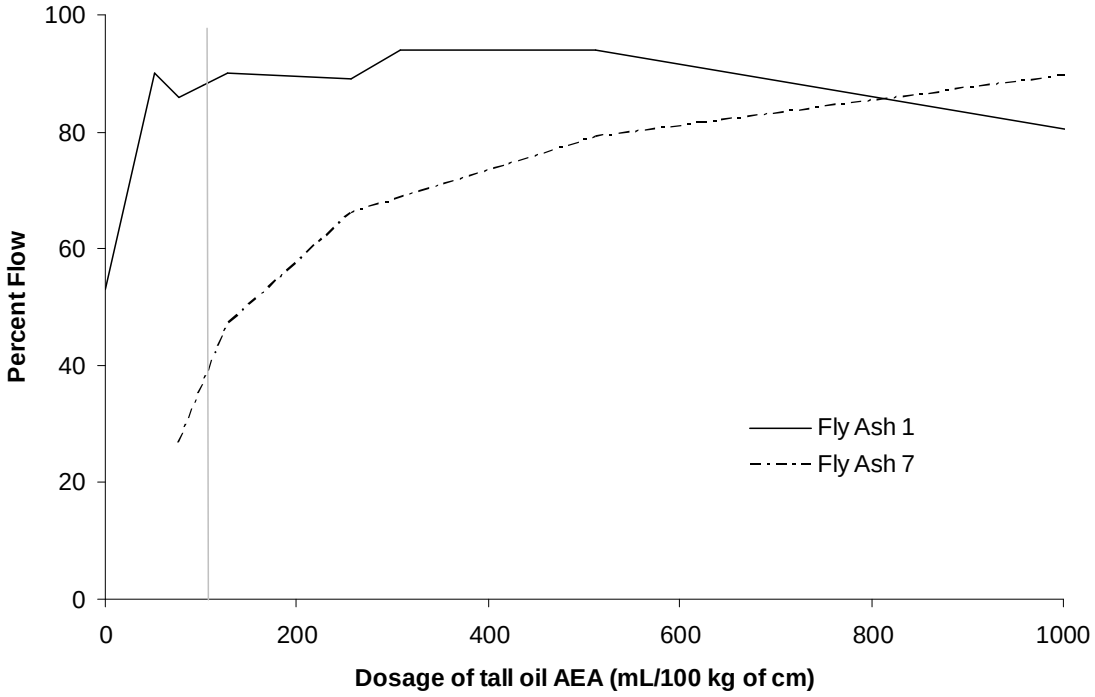


Fig. 3.5 – Flow of a modified mortar mixture with various dosages of tall oil AEA.

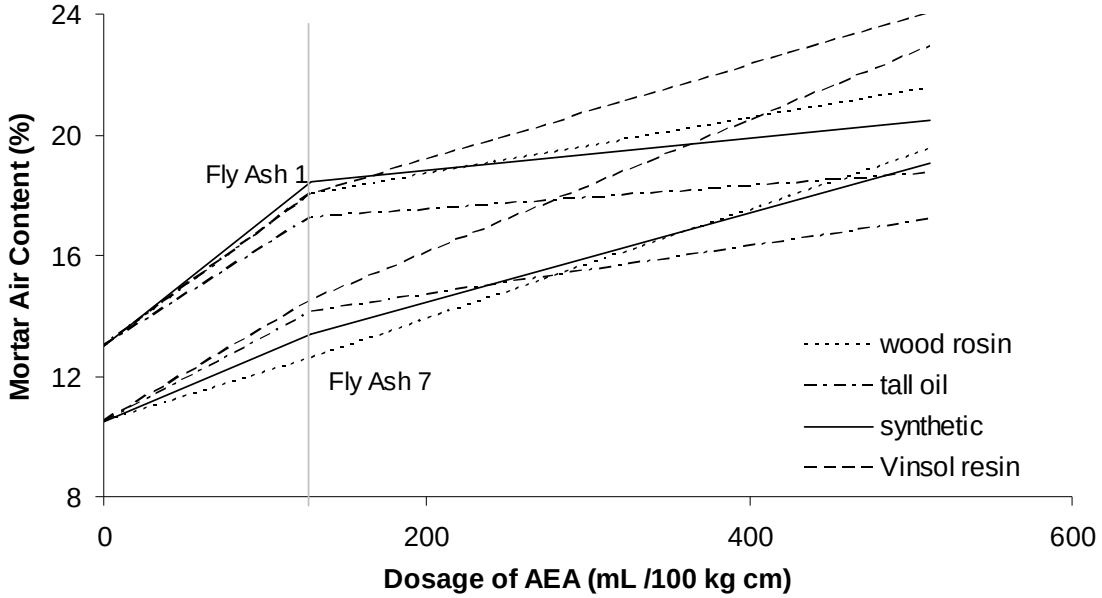


Fig. 3.6 - The air content of a modified ASTM C 311 test with various AEA at a dosage of 0, 128, and 512 mL/100 kg of cm.

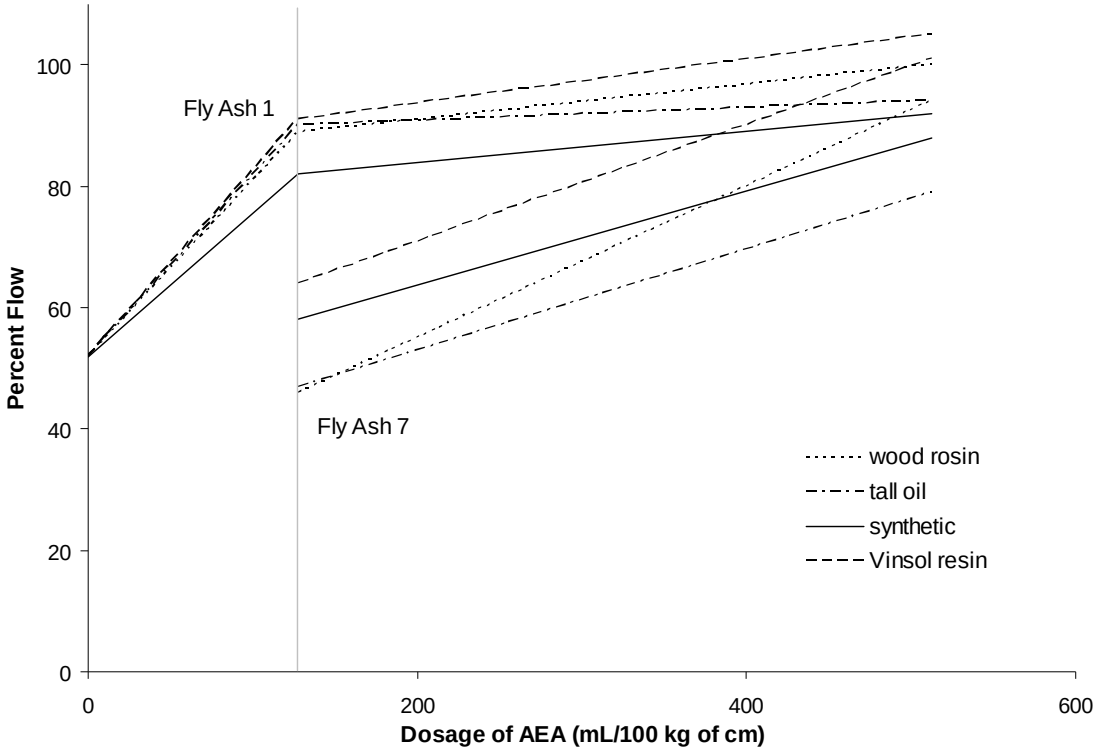


Fig. 3.7 - The flow of a modified ASTM C 311 test with various AEA at a dosage of 0, 128, and 512 mL /100 kg of cm.

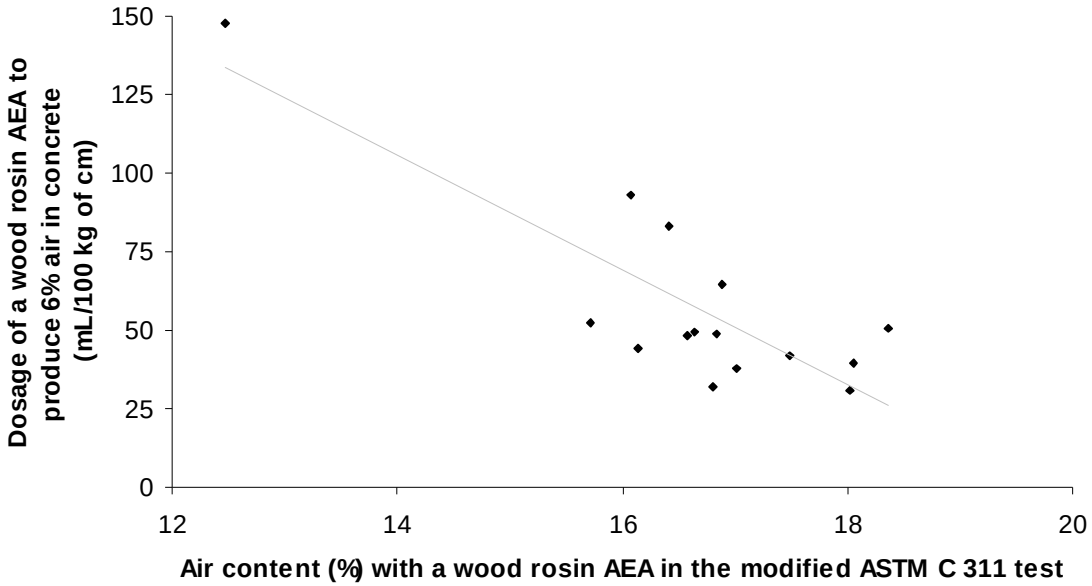


Fig. 3.8 – A comparison between the results of the modified ASTM C 311 test and the dosage of wood rosin AEA in concrete to produce 6% air for 15 different fly ashes.

Chapter 4: Determining the Air-Entraining Admixture Dosage Response From a Single Concrete Mixture

Abstract

Currently there is no standardized test method to determine the interaction of the ingredients of a concrete mixture with a dosage of air-entraining admixtures (AEA). Typically, to investigate the AEA demand multiple concrete mixtures are made with varying dosages of AEA and the resulting air contents are measured. This method is not ideal as it is time consuming, uses large amounts of material, and allows several variables to change that could cause changes in the dosage response of the mixture. A method is presented that is able to measure the air content of a mixture through a correlation between the gravimetric (ASTM C 138) and pressure method (ASTM C 231) with only minimal changes to the volume of the mixture. This allows the AEA demand to be determined from a single concrete mixture rather than sequential mixtures. Testing results are also provided for concrete mixtures containing fly ashes with various AEA demands. These mixtures are evaluated for changes in AEA demand with water reducer (WR), mixing temperature, fly ash replacement level, and type of AEA.

4.1 INTRODUCTION

While there are several existing methods available to design a concrete mixture, all of them require making a trial mixture with the actual materials to verify the assumptions of the design method and to make any adjustments to the mixture. One issue that is not able to be easily answered with a single trial mixture is the response of the mixture to admixture dosage.

One admixture whose dosage is exceptionally difficult to characterize in a concrete mixture is air-entraining admixture (AEA). The addition of AEA during the mixing of concrete is a common method to provide concrete with resistance to salt scaling and freezing and thawing. There are a large number of variables that have the

ability to affect the air void system in concrete. Some of these include: cement chemistry, mixture water chemistry, aggregate gradation, supplementary cementitious materials (SCM) and other chemical admixtures (Whiting and Stark, 1983).

The current method of examining the response of a mixture to AEA is to prepare several trial batches with different dosages of AEA and then examine how the mixtures respond. This method is useful as it allows a direct observation of how these materials perform in concrete. In creating each one of these mixtures it is difficult to ensure that no unintentional variables have been introduced that can affect the results. Any of the following changes between batches could cause differences in results: moisture content of the aggregates, batch weights, sand gradation and mixing methods.

Practitioners and researchers would benefit considerably if a new method to determine the response of a mixture to AEA demand could be developed from a single batch of material. This would minimize the efforts to create the mixtures, while also removing the variability between mixtures. This method must allow the mixture to be evaluated without substantially changing the volume of the mixture in order to keep the mixing action at a constant level, as this could lead to changes in the resulting air content. Furthermore, this method must provide a good correlation to individual mixtures cast at discrete dosages of AEA.

4.1.1 Methods of Measuring Air Content in Concrete

To examine the total volume of air content in fresh concrete there are currently three common methods: gravimetric (ASTM C 138), pressure (ASTM C 231), and volumetric (ASTM C 173).

In the gravimetric method a container of a known volume is filled with the concrete to be investigated and consolidated in a standard manner. This volume of concrete is then weighed and from this weight, material properties, and theoretical batch weights the total volume of air can be calculated for that mixture. Some problems with this method have been pointed out by Roberts (2006). These problems include the need

for very accurate batch weights, material properties, and moisture content. It is difficult, in the laboratory or in the field, to get an accurate measure of air content with the gravimetric method. One advantage to this method is that it allows the concrete utilized in the test to be reused. This concrete can either be returned to the mixer or used for other tests. Care should be taken though to return this material to the mixer and agitating the mixer so that the material is well mixed.

The pressure and volumetric methods of measuring air content do not rely on an accurate characterization of the mixture materials and instead attempt to directly measure the amount of air in the mixture. However, both of these methods require water to be added to the concrete specimen. This addition of water changes the water content and forces the concrete analyzed in the test to be discarded. When using either of these methods the volume of the mixture that is being investigated will decrease in size. While this size change is not a concern when a large truck or central batch mixer is used, this volume decrease is significant for a laboratory mixer. By using either one of these methods to evaluate the air content of a laboratory mixer it is likely that the mixture volume will change from 10% to 25%. Therefore, after investigating the air content of the laboratory mixture the remaining material would have to be discarded if the dosage did not yield the required air content.

Criticisms have been made of both the pressure and volumetric methods of measuring the air content of concrete. However, the pressure meter seems to be the test that is most widely used to evaluate the air content of fresh concrete. For this reason this test method was used in this research. The methods presented though should work accurately for either meter but was not verified with this work.

4.1.2 Combining the Gravimetric and Pressure Method

If one were able to accurately measure the air content of a mixture while holding the volume of the mixture constant then it would be possible to prepare a single concrete

mixture and evaluate how the air content of that mixture changes as AEA is added. However, none of the existing methods, at least individually, allow this to happen.

By combining the results of a gravimetric and either the pressure or volumetric method, one should be able to correlate the volume of air in a mixture to a measured density. Assuming that both of these tests are preformed properly then the unknowns in the gravimetric test are no longer significant as the air-void content has been tied to the density of the mixture. After this correlation is made, the air content of the mixture can be evaluated by only monitoring changes in the density of the mixture as long as no other variables are allowed to change.

By using the gravimetric method to monitor the density change and then returning the materials to the mixer it allows successive AEA dosages to be made to a mixture and the resulting changes in the air content to be measured. A method similar to this is suggested by Roberts (2006) to verify the results of the pressure method on several successive concrete batches with the same mixture design.

4.1.3 Objectives

The objectives of this work are to develop a test method that is able to utilize a single concrete mixture to determine the impact on AEA demand of the ingredients. This test method will then be utilized to investigate the impact of several variables commonly reported to cause an impact on the AEA demand of a concrete mixture. While past literature does exist about the impact of several of these variables on the ability to entrain air in concrete this data is presented to show the abilities of this test to investigate the performance of different variables in a concrete mixture.

4.2 EXPERIMENTAL

4.2.1 Materials

In all of the mixtures presented in this paper, Type I/II cement (conforming to ASTM C 150) was used, with an equivalent alkali content (Na_2Oeq) of 0.53 and a Blaine

fineness of 3630 cm^2/g. The phases of the cement are reported in Table 4.1 as determined by a Rietveld quantitative x-ray diffraction (RQXRD) (Rietveld, 1969; Stutzman, 1996) completed with the Topas Academic Software. The aggregates used in the mixtures were locally available river gravel and sand that are commercially used in concrete. All of the AEAs were obtained from commercial sources and meet ASTM C 260. The WR used in this research met the requirements of ASTM C 494 as a type A and D.

In this paper the AEA demand for 17 different fly ashes (all meeting ASTM C 618) were investigated. Material properties for these fly ashes can be found in Appendix C. However, additional testing was completed on a subset of three fly ashes. These three fly ashes (all ASTM C 618, Class F) were chosen as they exhibited drastically different AEA demands in prior laboratory testing. Fly ashes 6 and 7 were obtained from the same source; however, fly ash 6 had been treated with a sacrificial surfactant to improve the AEA demand in concrete (Hill et al. 2004). No information was provided by the manufacturer about the amount of sacrificial surfactant that was added to the fly ash. Therefore, all results for fly ash 6 are likely dependent on the amount of this additive. If the concentration is changed then the results for fly ash 6 may also change. An oxide analysis completed with x-ray fluorescence spectroscopy and loss-on-ignition (LOI) measurements from ASTM C 311 is reported in Table 4.2 for each of the three fly ashes.

4.2.2 Concrete Mixture Methodology

The following methodology was used to investigate the response of a single concrete mixture to increases in AEA dosage. Initially, a 64-L batch of concrete was prepared in a 85-L drum mixer. The mixture used a 0.45 w/cm with 335 kg/m^3 (equivalent to 6 sacks of cement) of total cementitious materials (cm), with a 20% replacement of the fly ash (by mass of cement). Proportions for the mixture can be found in Table 4.3.

All of the materials for the mixture were stored at 23°C for 24 hours prior to mixing to keep the mixing temperature constant. Coarse and fine aggregates were brought in from the stock piles and individually mixed. A moisture correction for each was used to adjust the batch weights. The rock and sand were added to the mixture first and 2/3 of the mixing water. The mixture was agitated for one minute. Next the cement, fly ash and the remaining mixing water were added and mixed for three minutes. At this point, the mixer was stopped and any material gathering on the sides or back of the mixer was removed. During the final three minute mixing period a normal water reducer (WR) was added to the mixture in either a desired dosage or to bring the mixture to a desired slump (ASTM C 143). It was found for the materials used in this study that there was interplay between the efficiency of the AEA and the WR dosage used. In order to compare results between mixtures it was necessary to have mixtures that had a similar WR dosage and workability. These issues are discussed in detail in later sections.

The following samples were taken after the mixing was completed: a 7-L sample for a gravimetric test, a slump test, and a 1-L rectangular prism for hardened air void analysis. The air content of the gravimetric sample was determined by the pressure method establishing the relationship between the air content and the density of the mixture. The concrete used for the slump test was returned to the mixer leaving the volume of the batch equal to 56-L. Next a commercially available AEA was added to the mixture and mixed for three minutes. Slump and gravimetric measurements were taken and the concrete was returned to the mixer. A 1-L rectangular prism was also taken for hardened air void analysis. These steps were repeated in regular dosage increments and the gravimetric measurement was taken until the change in the density from the initial sample was approximately 6%. A final slump, air content by the pressure meter, and rectangular prism were taken from the mixture.

Throughout this paper the terms slump and workability have been used interchangeably. However it has been shown that the slump test, although widely used

because of its simplicity, is not able to accurately measure the plastic viscosity of a mixture (Tattersall and Banfill, 1983). Plastic viscosity has been shown to be an important variable in the rheology of concrete. Furthermore, ASTM C 143 reports that the single operator and multilaboratory acceptable range for a slump of 85 mm to be +/- 25 mm. This would indicate that the test may not be precise enough to determine the workability differences in the mixtures investigated. Had this study been completed using a method of measuring the rheology of the concrete instead of the slump test, then a better understanding of the relationship between a rheological parameter of the mixture, WR dosage and AEA demand may have been determined.

4.3 RESULTS AND DISCUSSION

By using the combination of results from the gravimetric and pressure methods it was possible to measure the initial density and total air content of a mixture and correlate them. This correlation was then used to monitor the density change in the mixture with increased dosages of AEA and mixing. The percent change between the initial density and the density being investigated for a given AEA dosage was assumed to be equal to the change in air content for the mixture. Since these measurements were able to be made without significantly decreasing the volume of the mixture, additional AEA dosages could be added to the mixture and the mixture could be re-evaluated. After the unit weight of the concrete mixture had changed by approximately 6%, a final pressure meter reading was taken from the mixture. The predicted air content at that AEA dosage from the initial pressure meter reading and the unit weight measurements were compared to the final pressure meter reading. The difference between these values were found and the measured results were adjusted to correct for this difference. This correction was made by dividing the difference by the number of measurements and making an equal adjustment to each of the measurements. This difference between the air content predicted and measured by the final pressure meter reading was typically less than 0.5%. A linear trend was then fit to the estimated air content versus the AEA dosage. In Fig.

4.1 a sample data set is shown for this method. This figure shows a discrete set of data points with a linear trend fit to the data. Several data points are also shown from individual mixtures that did not use the multiple dosage method to compare the difference. By using the linear trend one is able to compare the AEA demand between different concrete mixtures. This comparison can be made by comparing the amount of AEA required to produce a certain air content or the slope of the trend-line provides information on the change in air content for a given dosage of AEA. In this chapter the dosage of AEA required to produce an air content of 6% was used. A value of 6% air content was chosen as it is a common value required in specifications for concrete.

It was found for these mixtures that even though the air content changed by 7% with increased AEA dosage, the slump of the mixture did not increase by more than 25 mm. It is expected that different results may be obtained with the same materials if the mixture were prepared with different mixing durations, speeds, or energy per unit volume of mixture. Nevertheless, this method allowed a useful comparison for the response of concrete mixtures to AEA dosages.

4.3.1 Validation

The average correlation coefficient (r^2 value) for the linear fit to the discrete air contents measured from a single mixture for more than 130 concrete mixtures created with this method was 0.98, with a standard deviation of 0.04. This shows that the response of the mixture to increases in AEA dosage as measured by this method seems to consistently fit a linear trend. In order to examine how well this method is able to represent the performance of mixtures made with individual dosages of AEA, a comparison was made between the air content measured in single dosages and the values predicted by the linear trends from the mixtures of multiple doses. This comparison was made between mixtures that contained different AEAs and fly ashes. The results of this comparison are shown in Table 4.4. The measured air contents closely match those predicted. The largest difference in air content was found to be 0.8% between the two

methods with an average difference of 0.0% and a standard deviation of 0.4%. This shows that there is a good correspondence between the air content measured in several individual mixtures and the air content predicted by correlating the density and air content determined by the pressure method in a single mixture and using multiple dosages of AEA.

4.3.2 Effect of Water Reducer Dosage on Air-Entraining Agent Dosage

In order to investigate the affect of the WR dosage on AEA demand for a fly ash concrete mixture with wood rosin AEA, several mixtures were prepared with different dosages of WR. The AEA demand was determined in a single mixture as previously described. The results are shown in Table 4.5 and in Fig. 4.2. One would expect that as the WR dosage was increased between mixtures that the slump of the mixture would also increase. This trend follows for fly ash 1 and 7. Even though the slump of the mixture does not correspond to the WR dosage directly, it seems the AEA dosage required in concrete to produce 6% air content shows a good correlation. As shown in Table 5 as the WR dosage increases, the AEA demand to produce 6% air content in concrete decreases for both fly ashes 1 and 7.

These results suggest that if two mixtures are to be compared to one another then it is more important to have a similar WR dosage in the mixture then a similar slump. However, in preliminary testing it was found that a minimum workability was needed to efficiently entrain air in concrete. Other research suggests that when the workability of a mixture becomes too high then it is difficult to stabilize the entrained air bubbles (Dodson, 1990). Because of this it was decided that the concrete mixtures should have a slump between 50 and 100 mm to be accurately investigated.

4.3.3 Evaluation of AEA Demand of Fly Ash Concrete

By using a correlation between the pressure and gravimetric methods, one is able to evaluate the AEA demand of a fly ash concrete in a single mixture. These differences

in AEA demand can occur for any number of reasons, but are usually attributed to the amount of carbon in the fly ash remaining after the burning process (Gebler and Kleiger, 1983). Reports of the variability of AEA demand in fly ash concrete have increased as the coal fired power plant sources have been required to reduce emission levels (Freeman et al. 1996; Kulaots 2004; Hill and Folliard 2006). To reach these reduced emissions several modifications to the coal burning process can be made. It is unclear how each of these modifications impact the AEA demand of fly ash in concrete, and more research is needed before conclusions can be made. However, the ability to assess the AEA demand of a fly ash concrete mixture has been important in the past and continues to become more relevant.

This method was used to evaluate the AEA demand of 19 different fly ashes that were produced in power plants in Texas and the results are reported in Table 4.6. In order to make a fair comparison between fly ash samples it was decided that the slumps and WR should be within a certain range. Each mixture was prepared with a target WR dosage between 45 and 85 mL/100 kg cm and target slump between 50 and 100 mm. However, the WR dosage had to be adjusted for two of the fly ash mixtures due to insufficient slump of the concrete caused by differences in water demand. Both of these mixtures required dosages of over 110 mL/100 kg cm and have been reported with an asterisk in Table 4.6. These mixtures contained fly ashes that were treated with a sacrificial surfactant to decrease the AEA demand of the fly ash. It is possible, but not certain that this treatment contributed to this increase in water demand observed.

4.3.4 Effects of Mixing Temperature, Percent Fly Ash Replacement, and AEA Type on AEA Demand

In this section the effects of mixing temperature, percent fly ash replacement, and AEA type are reported for three fly ashes. The results are contained in Tables 4.7 and 4.8. For each of these mixtures the WR dosage was held constant where possible in order to investigate the effects of each variable. Care should be taken in extrapolating

comparisons beyond what is presented in the table as the WR dosage was not held constant between all variables due to the large differences in water demand between the mixtures. Ratios larger than 1 in Tables 4.7 and 4.8 show an increased AEA demand.

4.3.4.1 Mixing Temperature

To compare the effects of different mixing temperatures on fly ash concrete with different AEA demand, mixtures were prepared with the constituent materials initially conditioned to 10, 23, and 32^{o} C. For each mixture, the AEA demand was determined by the dosage of AEA required to produce 6% air content in the mixture. These results are presented in Table 4.7. In each one of these comparisons a constant WR dosage was used for all of the mixtures containing a given fly ash and the results of each mixture is compared back to a mixture at 23^{o} C.

It appears that the change in temperature had little effect on the AEA demand for mixtures with fly ash 1. However, the AEA demand decreased for the mixtures with fly ashes 6 and 7 as the mixing temperature increased. Past research has suggested that as the mixing temperature increases, the efficiency of the AEA decreases (Gay, 1985). The response of the fly ash with the sacrificial surfactant (fly ash 6) seemed more sensitive to the temperature than the others investigated.

4.3.4.2 Fly Ash Replacement

The amount of wood rosin AEA required to produce 6% air in concrete for mixtures utilizing fly ashes 1, 6 and 7 at replacement levels of 20%, 35%, and 50% is shown in Table 7. Fly ash 1 shows a reduction in the amount of AEA demand required in the mixture as a higher fly ash replacement is used. For fly ash 6, a complete data set was not obtained as the slump of the mixture at a 20% replacement level was not comparable to the mixtures at 35% and 50% replacement and WR dosage used. However, there was very little change in the AEA demand as the amount of fly ash in the mixture increased. This behavior is different than what was observed with mixtures

containing fly ash 7 as the AEA demand increased as the amount of fly ash replacement increased. This increase in AEA demand was not linear.

4.3.4.3 Response of Fly Ash Concrete to Different AEAs

Several different commercial AEAs were used in concrete mixtures with the different fly ashes to investigate the AEA demand. The results are shown in Table 8. For all of the AEAs investigated fly ash 1 showed the lowest AEA demand, fly ash 6 showed more AEA demand than fly ash 1 and fly ash 7 showed the highest AEA demand. When comparing the difference in AEA demand between fly ashes 1 and 7, it was determined that the largest change was for the wood rosin AEA and the smallest change was for the synthetic AEA. The AEA demand for the tall oil and Vinsol resin fell in between these values but were closer to the values for the synthetic AEA at 3.47 and 3.57 times higher then the AEA demand for fly ash 1. When investigating the change in AEA demand between mixtures containing fly ashes 1 and 6 it was found that the wood rosin still showed the highest change in demand and the Vinsol resin showed the least. It should be noted that a mixture with fly ash 6 and the synthetic AEA was not investigated.

4.3.4.4 Comparison of Results for Fly Ash 1, 6, and 7

One significant finding from the testing was that fly ash 6 behaved notably different then fly ashes 1 and 7 in the testing. As reported earlier fly ash 6 is a sample from the same source as fly ash 7 but was treated with a sacrifical surfactant of an unknown dosage to reduce the AEA demand of the fly ash. As can be seen from the results that this treatment does consistently reduce the AEA demand of the concrete mixture over the variables investigated when compared to fly ash 7. Other notable behavior is that fly ash 6 seems to show a greater change in AEA efficiency when the mixing temperature is raised. The material also shows a consistent dosage requirement in concrete as the percent replacement of the fly ash is increased with respect to the cement. This is significantly different to the behavior of fly ash 7 as the AEA demand of this

mixture increased non linearly with fly ash replacement. The significant decrease in AEA efficiency with increase in temperature, and the behavior of the AEA demand to remain constant with increasing levels of fly ash replacement are likely attributable to the sacrificial surfactant that was added to the fly ash.

The mixtures containing fly ash 1 at different replacement levels show a decrease in AEA demand with increasing replacement levels of fly ash. Fly ash 1 was shown to have a very low AEA demand when used at 20% replacement in concrete. When larger replacements are used in a mixture then one would expect the workability to increase. This increase in workability appears to have caused a decrease in the AEA demand as it has made it easier to entrain air in the mixture.

Fly ash 7 was found to consistently require a higher AEA dosage then either fly ash 1 or 6 and was found to have the highest of the 19 fly ashes investigated. This larger dosage requirement is likely caused by increased levels of high activity carbon in fly ash 7. This increase in high activity carbon could also cause an increase in variability in slump obtained by the different mixtures shown in Table 5. The high activity carbon could lead to a reduced efficiency of the WR or an increase in fineness of the mixture that affected the workability of the mixture.

From the results of the different AEAs used in combination with the different fly ashes it appears that the change in AEA demand between fly ash 1 and 7 was very similar for all of the AEAs investigated except for the wood rosin AEA. This suggests that the wood rosin AEA may be more sensitive to changes in AEA demand (from fly ash) than the other commercial AEAs investigated with the normal WR used in this study.

As a whole, this study shows that every fly ash is different, and its response to changes in dosage, temperature, and AEA dosage/type can vary considerably from source to source (and presumably from time to time for a given source). This reinforces the need to have available simple, but accurate, test methods to evaluate the AEA demand for a given concrete mixture containing a particular fly ash. The work presented in this

chapter, coupled with other work presented in this dissertation and parallel efforts at Cornell University, are aimed at providing such tools to allow for accurate assessments of any fly ash source, with regard to AEA dosage response.

4.4 CONCLUSIONS

This paper has presented a method to produce an AEA dosage response curve for a concrete mixture while only using a single mixture. The method was then compared to the AEA dosage response of several sequential mixtures and the results were found to be closely comparable for air contents up to 7%. Next, the method was utilized to build a large data set to compare several variables that affect the AEA demand of concrete that are not easily measurable by using single mixtures. These include: effects of WR dosage on AEA demand, ranking the AEA demand of several fly ashes, mixing temperature, fly ash replacement, and comparison of different commercially available AEAs. This data set provides insight into how mixing temperature, percent fly ash replacement and AEA type affects fly ash concrete with high and low AEA demand as well as a fly ash utilizing a commercially available sacrificial surfactant to reduce the AEA demand in fly ash concrete.

The results of this paper suggest:

- The WR used in this paper showed the ability to reduce the wood rosin AEA demand in fly ash concrete with increasing dosages.
- A sacrificial surfactant that is used on fly ash with high AEA demand can decrease the AEA demand of fly ash concrete
- The mixing temperature had a larger impact on the AEA demand of a fly ash treated with a sacrificial surfactant then the other fly ash mixtures investigated
- As the percent fly ash replacement increases in a concrete mixture the AEA demand in fly ash concrete decreased if the AEA demand of the fly ash was low or increased if the AEA demand of the fly ash was high. This increase occurred in a nonlinear fashion.

- The AEA demand of fly ash treated with a sacrificial surfactant did not change as the percent fly ash replacement increased
- A wood rosin AEA is the most sensitive of the AEAs examined to a fly ash with a high AEA demand in concrete

Table 4.1 – Composition of the Type I/II cement as determined by RQXRD

phase	percentage
C_3S	68.0
C_2S	15.7
C_3A	2.7
C_4AF	8.7
gypsum	1.3
$CaCO_3$	2.6

Table 4.2 – Oxide analysis and LOI data for three fly ashes

Fly Ash Name	1	6	7
Silicon Dioxide (SiO_2), %	56.18	52.07	52.04
Aluminum Oxide (Al_2O_3), %	20.37	23.65	23.75
Iron Oxide (Fe_2O_3), %	6.77	4.55	4.59
Sum of SiO_2, Al_2O_3, Fe_2O_3, %	83.32	80.27	80.38
Calcium Oxide (CaO), %	9.95	12.76	12.63
Magnesium Oxide (MgO), %	2.55	2.02	2.01
Sulfur Trioxide (SO_3), %	0.53	0.78	0.79
Sodium Oxide (Na_2O), %	0.47	0.31	0.28
Potassium Oxide (K_2O), %	1.08	0.80	0.81
Total Alkalies (as Na_2O), %	1.18	0.84	0.81
ASTM C 618 Classification	F	F	F
LOI (ASTM C 311)	0.12	0.79	0.79

Table 4.3 – Concrete Mixture Design

Components	Mass (kg/m^3)
Cement	268
Fly Ash	67
Coarse Aggregate	1098
Fine Aggregate	742
Water	151

Table 4.4 – Comparison of measured air content in mixtures with single dosages of AEA and that predicted by a mixture using multiple dosages of AEA.

Fly Ash	AEA Product	Slump	normal WR	AEA	Percent Air Content		
		(mm)	mL/100 kg cm	mL/100 kg cm	Measured	Predicted	Difference
1	tall oil	89	170	50	**5.7**	**5.2**	**0.5**
1	tall oil	89	170	100	**7.8**	**8**	**-0.2**
1	wood rosin	70	44	27	**6**	**6**	**0**
1	wood rosin	51	46	47	**6.2**	**6.3**	**-0.1**
6	synthetic	76	166	36	**3.2**	**3.2**	**0**
6	synthetic	76	166	89	**5.6**	**5.4**	**0.2**
6	synthetic	76	166	140	**7.3**	**7.5**	**-0.2**
6	tall oil	70	169	194	**6**	**5.3**	**0.7**
6	tall oil	76	169	344	**8.5**	**9.3**	**-0.8**
6	tall oil	70	169	125	**4.4**	**4.6**	**-0.2**
6	wood rosin	89	83	30	**2**	**2.6**	**-0.6**
6	wood rosin	89	83	93	**5.4**	**5.2**	**0.2**
7	wood rosin	51	108	32	**3.2**	**3.2**	**0**
7	Vinsol resin	95	33	124	**4.5**	**4.5**	**0**
15	wood rosin	76	72	44	**5.3**	**5.4**	**-0.1**
15	wood rosin	76	72	69	**7.3**	**7.2**	**0.1**
						average	**0.0**
						standard deviation	**0.4**

Table 4.5 –AEA demand for two fly ashes with different dosages of WR.

fly ash	slump (mm)	AEA demand[y] (mL/100 kg cm)	WR (mL/100 kg cm)
	51	62	0
	102	53	44
	102	31	84
1	102	35	98
	121	29	102
	102	28	169
	127	37	194
	64	238	0
	83	192	46
	89	139	83
7	102	112	84
	102	108	103
	70	95	167
	83	78	196

y - Dosage of wood rosin AEA required to produce 6% air content in the mixture. These values are interpolated from the dosage response curve.

Table 4.6 – A ranking of several fly ashes commercially used in concrete by the AEA deamand from the single mixture method

fly ash	slump (mm)	WR (ml/100 kg cm)	AEA demand[x] (mL/100 kg cm)
1	100	83	**31**
23	95	45	**32**
19	95	66	**34**
11	70	81	**36**
27	64	45	**38**
10	95	46	**39**
8	89	64	**42**
2	76	51	**44**
9*	57	132	**44**
25	64	58	**48**
15	95	68	**49**
20	70	46	**49**
5	64	46	**50**
16	76	72	**52**
26	89	48	**64**
4	83	47	**83**
14	83	50	**93**
6*	57	111	**138**
7	83	71	**147**

* These mixtures required high dosages of WR to obtain an acceptable slump. This increase in WR could cause a response in the AEA demand of the mixture.
[x] – Dosage of wood rosin AEA required to produce 6% air content in the mixture. The value is interpolated from the dosage response curve.

Table 4.7 – Effects of mixing temperature and fly ash replacement on AEA demand in concrete for three fly ashes.

	Fly Ash					
	1		6		7	
Details of Mixture	AEA Demand[A]	Ratio to Standard[B]	AEA Demand[A]	Ratio to Standard[B]	AEA Demand[A]	Ratio to Standard[B]
Mixing Temperature						
32°C	32	1.03	187	1.35	224	1.16
23°C	31	1.00	138	1.00	192	1.00
10°C	29	0.94	60	0.43	80	0.42
Fly Ash Replacement						
50%	44	0.71	203	-	368	1.54
35%	40	0.65	196	-	267	1.12
20%	63	1.00	-	-	239	1.00

[A] – The amount of wood rosin AEA (mL/100 kg cm) required to produce 6% air in concrete. The value is interpolated from the dosage response curve.
[B] – The ratio of the AEA demand for the variable being investigated and fly ash compared to a mixture prepared with wood rosin AEA at 23°C, with a fly ash replacement of 20%, and with a 0.53 Na_2O_{eq} cement.
Note: The WR dosage was held nearly constant between fly ashes for each variable investigated. However WR dosage was not able to be held constant for the entire table and so comparisons should not be taken past those presented.

Table 4.8 – Effects of AEA type on AEA demand in concrete for three fly ashes.

	Fly Ash					
	1		6		7	
AEA	AEA Demand[A]	Ratio to Standard[B]	AEA Demand[A]	Ratio to Standard[B]	AEA Demand[A]	Ratio to Standard[B]
Synthetic	33	1.00	-	-	104	3.12
Tall Oil	67	1.00	181	2.72	231	3.47
Vinsol Resin	40	1.00	73	1.84	142	3.57
Wood Rosin	29	1.00	95	3.32	147	5.14

[A] – The amount of wood rosin AEA (mL/100 kg cm) required to produce 6% air in concrete. The value is interpolated from the dosage response curve.

[B] – The ratio of the AEA demand for the variable being investigated and fly ash compared to a mixture prepared with wood rosin AEA at 23°C, with a fly ash replacement of 20%, and with a 0.53 Na_2O_{eq} cement.

Note: The WR dosage was held nearly constant between fly ashes for each variable investigated. However WR dosage was not able to be held constant for the entire table and so comparisons should not be taken past those presented.

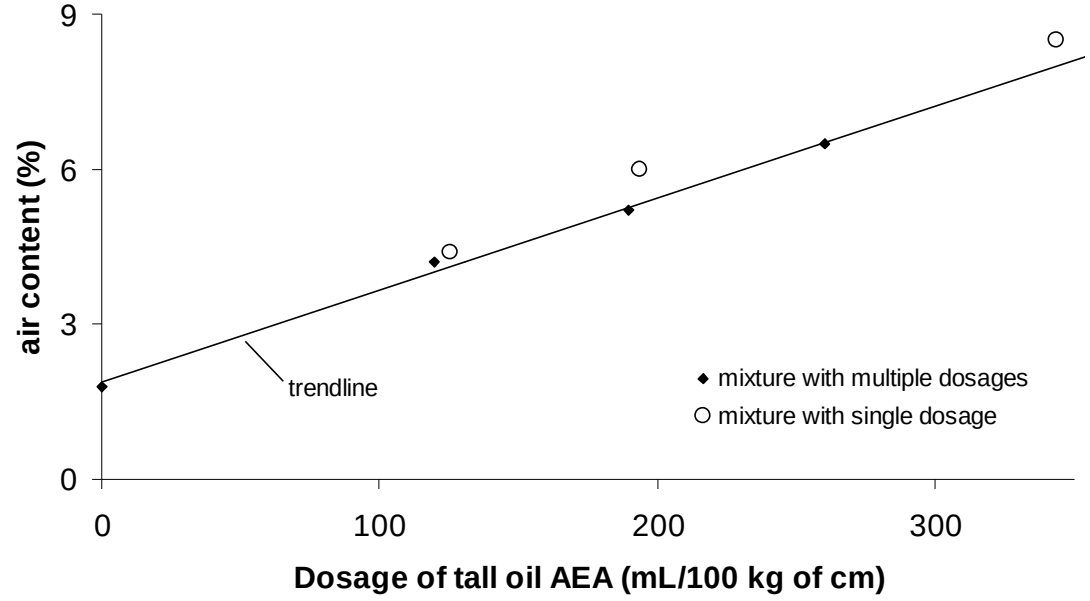


Fig. 4.1 – Air content versus AEA dosage from single mixture method compared to several individual mixtures with a trendline fit to the single mixture method results.

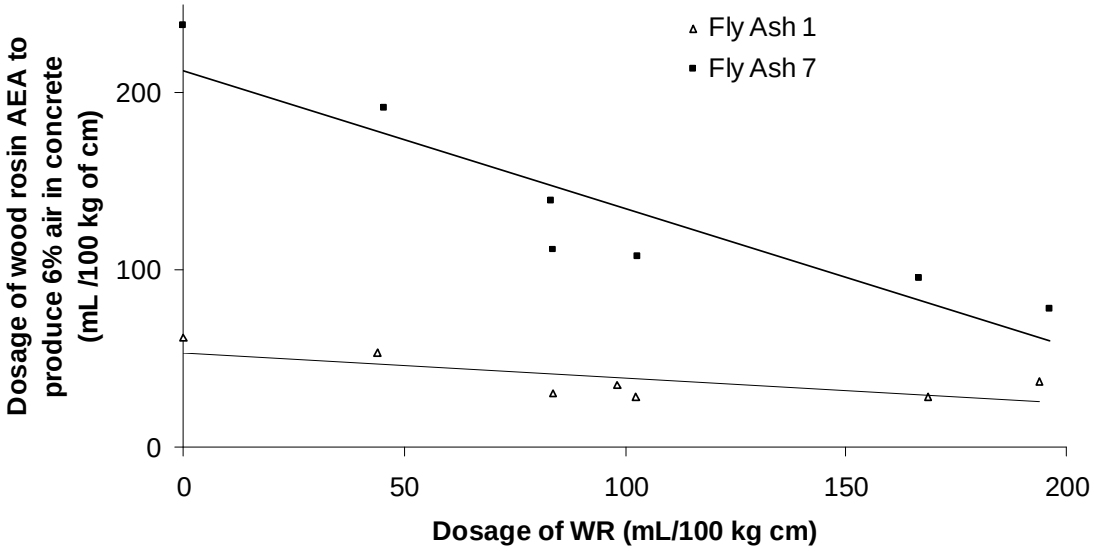


Fig. 4.2 –AEA demand interpolated from single mixture method for two different fly ashes with different dosages of WR.

Chapter 5: Investigation of the Frost Resistance of Concrete Through Measurement of Fresh and Hardened Properties and Resistance to Rapid Freezing and Thawing Cycles

Abstract

Although it is widely understood that the size and spacing of the air-void system inside concrete is crucial to providing freeze-thaw durability, it is common for specifications to instead require measurement of the total air volume in fresh concrete. This practice is followed because there are no established or standard methods to evaluate the size and spacing of the air-void system in fresh concrete. This chapter highlights some of the challenges of using a pressure method (ASTM C 231) and a commercial Air-Void Analyzer (AVA) to evaluate the air-void parameters of fresh concrete. Correlations are made between these two methods, hardened air-void analysis, and rapid freeze-thaw testing (ASTM C 666).

5.1 INTRODUCTION

In order to produce concrete that is durable to exposure to moist freezing and thawing environments, it is well understood that an adequate air-void system must exist in the paste of the concrete. This air-void system is traditionally produced in concrete by adding an air-entraining agent (AEA) during mixing. This admixture gathers at the interface between the air and water and reduces the surface tension. This alteration of the surface tension improves the probability of trapping and stabilizing air-voids or forming smaller bubbles when a larger bubble is sheared during mixing (Powers, 1968). The number, size, and distribution of these small air voids are currently thought to be the key parameters in imparting freeze-thaw durability to concrete.

The most common methods to directly evaluate concrete durability in a cold climate are ASTM C 666 (resistance to rapid freezing and thawing) and ASTM C 672 (surface scaling resistance). ASTM C 666 and ASTM C 672 tests force a saturated

specimen into a harsh freezing environment and evaluate the damage to the specimen after several cycles of freezing and thawing. These tests have the ability to provide insight into the resistance of concrete to freezing and thawing. However, the results of these tests require months to obtain. Another common method of investigating the frost durability of a concrete is to microscopically investigate the air void system using a test described in ASTM C 457 (hardened air-void analysis). While this test does not require the months required by the previously mentioned tests, it is quite labor intensive.

The inability to obtain rapid results from these tests does not make them easy to use in construction specifications. Instead, specifications often require a satisfactory volume of air to be required in the fresh concrete. This air content is typically specified to be measured at the point of placement and consolidation. However it is commonplace to take these measurements at a different convenient time and place during the construction process. A myriad of methods exist to evaluate the total air content including tests described in ASTM C 231 (pressure method), ASTM C 173 (volumetric or "roller" meter), or ASTM C 138 (gravimetric method). While the method of evaluating the total volume of air in fresh concrete as a means for acceptance of materials is common, it has been shown in previous research that it is possible to obtain air-void parameters that are not satisfactory at air contents commonly specified (Saucier et al., 1991; Plante et al., 1989). Due to this lack of correlation between the fresh air content and hardened air-void parameters a method to better evaluate the air-void system in fresh concrete is needed. The Air Void Analyzer (AVA) is a device advertised to measure the air-void parameters in fresh concrete. This device was evaluated for this project and the results are then compared to air-void analyses and performance tests on hardened concrete.

5.1.1 Objectives

This chapter reports on laboratory testing performed to evaluate the air-void system in fresh concrete,as measured by pressure meter to obtain total air volume and by

the AVA to attempt to quantify air-void parameters, and hardened concrete, as measured by use of RapidAir457 system for measurement of key air-void parameters in hardened concrete) and compares these results to the performance of selected mixtures subjected to freeze-thaw cycles as per ASTM C 666. Only minimal emphasis was placed on evaluating frost resistance (ASTM C 666) as it was not the prime focus of this research project; however, a limited number of mixtures were cast and tested to focus on specific issues related to concrete with low specified air contents as these mixtures were identified as being particularly relevant in the state of Texas. Specifically, for paving mixtures, relatively low air contents are allowed (e.g., 3.5 to 4 percent total air, as per pressure or roller meter), and it was decided to evaluate mixtures in this low range of air content. Relevant issues that were addressed included (1) the use (or in actually, lack of use) of the aggregate correction factor when using the pressure meter to measure air at the jobsite; (2) the use of high dosages of water-reducing admixture that generate enough air to often pass the low air content specifications; and (3) the use of fly ash treated with a sacrificial surfactant to help offset high absorption tendency of carbon in ash.

5.1.2 Background

Background information is provided on the methods utilized in this research to evaluate the air-void system of different concrete mixtures.

5.1.2.1 Concrete Pressure Meter (ASTM C 231)

The concrete pressure meter is the most common method utilized to assess the total air-void content of concrete. This method uses a 7 L sample of concrete that is consolidated in a standard manner. The response of the sample to an increase in pressure is measured and the air content in the mixture is estimated by using Boyle's Law.

Questions have been raised about the inaccurate simplifying assumptions made in the test and the ability of the test to measure the air content in very small air-voids (Gay, 1982). However, numerical simulations by Hover (1988) have suggested that these

concerns are insignificant for the air-void distributions commonly found in concrete. This test method was used in this research despite some concerns because of its widespread use in industry.

One challenge in using the concrete pressure method is that the pressure changes used in the method force water to be displaced into the pores of the aggregate in the mixture. Because of this, an erroneously high air content is reported in the results of the test from this displacement of water. If the porosity of the aggregate becomes very high, as in lightweight aggregate, then the pressure method is not recommended to be used to measure the air content of the mixture. A method is outlined in ASTM C 231 that is intended to provide a correction for this aggregate-related issue – namely, the aggregate correction factor. Unfortunately this method is rarely utilized in the field as the results are dependent on aggregate type, moisture content, mixture proportions, and target air content of the mixture.

As stated previously the pressure method does not give any indication of the air-void size, distribution, and spacing, only the total volume of air contained in the concrete. However, past research has shown that as the air content of a mixture increases, the air-void system improves (Saucier, et al., 1991; Backstrom, et al., 1958; Klieger, 1952). Work done by Klieger (1952) examining the results from a large number of ASTM C 666 tests with different size aggregates suggested that an air content between 8% and 10% is required in the mortar fraction of concrete if it is to be durable against freezing and thawing damage.

Currently, ACI 201.2R-01 "Guide to Durable Concrete" and ACI 318-05 "Building Code Requirements for Structural Concrete" recommends that the acceptable volume of air in a concrete mixture should be based on the maximum nominal aggregate size in the mixture despite this parameter having nothing directly to do with the freeze-thaw durability of concrete. These suggested air contents are often adopted into specifications without realizing that this recommendation is made with the assumption

that the concrete mixture has been designed by the ACI 211 mixture design method. In ACI 211 the maximum nominal aggregate size is used to determine the total amount of water used in the mixture for a desired workability. This selection of water then leads to the total amount of cementitious materials based on the needed water-to-cementitious material ratio. Finally the volume of fine aggregate is chosen to fill the remaining volume in the mixture. Therefore, the maximum nominal aggregate size has some bearing on the percentage of mortar in a mixture designed by ACI 211. While this method can be used as a starting point it rarely produces a mixture that is optimized for use with local materials. If a mixture is not designed according to ACI 211, or if the mortar content of the mixture is adjusted during the trial batches, then the correspondence between the air content required in the mixture and the maximum nominal aggregate size is no longer meaningful. Furthermore, specifications are often written assuming that a larger aggregate size will be used for the construction of an element (e.g. pavement) when this might not be the case. Care should be taken to insure that an air content of at least 8% is provided in the mortar fraction of the concrete regardless of the aggregate size utilized.

5.1.2.2 Air Void Analyzer (AVA)

The AVA (Jensen, 1990) is a device for analyzing the air-void system in the mortar that uses a 20 cm^3 of mortar that has been extracted from concrete so as to exclude material larger than 6 mm. The analysis is performed by injecting the extracted mortar into the base of a column containing de-aerated water and a special blue liquid. In order for the test to be valid the temperature of the water column must remain between 21 and 25 ^oC and the air content in the concrete mixture must be between 3.5% and 10%. A stirring rod is used in the bottom of the column to agitate the mixture for 30 seconds. An inverted Petri dish is suspended in the water at the top of the column to catch the bubbles that rise upwards. The change in the buoyancy force on the Petri dish is monitored by a balance and computer with time. According to Stokes' Law, larger diameter bubbles rise

at a faster rate than smaller ones. Changes in buoyancy measured in the test at different time periods give an indication of the volume of different size air-voids. From these measurements, and from inputs provided by the user about the mortar and paste content of the mixture, an estimate is made of the air volume, size, and distribution in the concrete. The data produced by the AVA is manipulated mathematically so that it can be directly comparable to the results from a hardened air-void analysis.

The AVA's goals of providing a rapid measurement of the air-void size and spacing in fresh concrete are drastically needed in the concrete industry. However, the AVA and its ability to accurately generate a measurement of the air void system of the subject concrete has been called into question (Desai et al., 2006; Distlehorst and Kurgan, 2006; Magura, 1996). Despite its potential drawbacks, the raw data collected by the AVA is a fundamental property of the mixture that should provide some indication of the actual air-void size distribution in concrete. What remains to be seen is if and how this fundamental property is able to give an accurate indication of the air-void parameters in concrete.

5.1.2.3 Hardened Air-Void Analysis (ASTM C 457)

Currently the most common method to examine the air-void spacing and size distribution in concrete is hardened air-void analysis performed according to ASTM C 457. This method inspects the area of a hardened concrete slab that is cut from a larger element and polished until the voids are clearly observable with a stereomicroscope at a magnification that is between 50x and 125x. The edges of the voids should be clearly observable with no differences in relief between the paste and aggregate on the sample surface.

Two different techniques are described by this method: the linear traverse and modified point count methods. In the modified point count method, locations on the sample are analyzed at regular intervals. At each one of these points the location is categorized as to whether it is an aggregate, paste, or air void. In the linear traverse

method the area is investigated in a similar manner, but instead of investigating the sample at discrete points the specimen is analyzed by a continuous line or traverse. As the traverse covers the specimen the length of paste, aggregate, and air-void chords can be recorded. One advantage with the linear traverse technique is that it is possible to record the chord lengths of the air-voids intersected to determine the frequency of each chord size covered in the analysis. Both methods are able to provide general estimates of the air content and air void parameters of the area analyzed.

Two of the most common parameters used to assess the quality of an air-void system in concrete are the spacing factor and specific surface. Both of these parameters are not directly measured in the ASTM C 457 analysis and are instead estimated from the parameters measured in the analysis. The specific surface is a measure of the surface area of voids divided by their volume. A higher specific surface of two samples with equal volume of air indicates that there is on average a larger number of small air bubbles in the sample with the higher specific surface. The spacing factor is a parameter developed by Powers (1949) that estimates the average maximum distance from a point in the cement paste and an air-void. The reported precision of the method for samples prepared and measured in the same laboratory is 1.61% difference in the total air volume and a maximum error of 22.6% for the spacing factor (ASTM C 457). Even higher values are reported for samples prepared and analyzed in different laboratories. This implies that the sample surface preparation techniques has an effect on the results of the test. Recommended values for the specific surface (24 mm^2/mm^3) and spacing factor (0.200 mm) were obtained from a comparison of length change of specimens in freezing and thawing tests to the air void parameters in the hardened concrete from two different mixtures (Powers, 1954; Backstrom et. al, 1958). Publications since have investigated the performance of multiple of different concretes in the test method and a spacing factor in the hardened concrete between 0.200 mm and 0.250 mm (Ivey and Torrans, 1970).

5.1.2.4 Resistance to Rapid Freezing and Thawing (ASTM C 666)

The most common method of determining the freeze-thaw resistance of concrete is to subject saturated specimens to rapid freeze-thaw cycles and to monitor the degradation by monitoring the change in the relative frequency of the specimen (and/or length change) of the specimen. In ASTM C 666, concrete prisms are subjected to 300 temperature cycles between 5 and -18 ^{o}C with certain allowable rates of heating and cooling. There are two different procedures outlined in the test method. Procedure A, the procedure utilized in this research, specifies that the specimens are stored in a metal box and allowed to freeze and thaw while completely surrounded by water. Procedure B requires specimens to freeze in air and to thaw in water. The samples are measured at regular intervals and the change in the resonant frequency (ASTM C 215), and weight of the specimens is monitored. Typically, results from the test are reported as a parameter called the durability factor. This value is equal to the square of the ratio of the relative frequency after 300 cycles to relative frequency at 0 cycles. The failure criteria for the test is not specified in the method and is intentionally left open to interpretation. However, several admixture specifications (ASTM C 260, ASTM C 494, and ASTM C 1017) recommend that the reduction in the ASTM C 666 durability factor of a mixture with and without an admixture should not be more than 20%. If this criterion is used to evaluate the performance of a mixture in the ASTM C 666 test then the limiting durability factor would be between 70 and 80.

Concerns have been stated (Pigeon and Pleau, 1995) that the ASTM C 666 test is much more severe then would be expected in nature and that the difference in laboratory testing methods could provide increased variability in results. Furthermore, the period of freezing that the specimen experiences in the test is very short and may not be representative of actual freezing. Also, the test results are shown to be sensitive to the surface scaling of the specimen (Pigeon and Pleau, 1995). Despite all of these

drawbacks, this test continues to be widely used to evaluate the freeze-thaw durability of a concrete mixture.

5.2 EXPERIMENTAL

5.2.1 Materials

In all of the mixtures presented in this chapter, a Type I/II cement (as per ASTM C 150) was used, with an equivalent alkali content (Na_2Oeq) of 0.53 and a Blaine fineness of 3630 cm^2/g. The phases of the cement are reported in Table 5.1 as determined by a Rietveld quantitative x-ray diffraction (RQXRD) (Rietveld, 1969; Stutzman, 1996) completed with the Topas Academic Software.

The aggregates used in the mixtures were locally available river gravel, limestone and natural sand. All aggregates are commercially used in concrete. All of the AEAs were obtained from commercial sources and meet ASTM C 260. The water reducer (WR) used in the majority of this research met the requirements of ASTM C 494 (Type A and D). A midrange water reducer (MWR) was used in the mixtures containing a limestone aggregate meeting the requirements of ASTM C 494 as a type A and F. The product information sheet classifies the MWR as a lignosulfonate with triethanolamine.

The mixtures presented in this chapter were primarily cast with three different fly ashes (all meeting ASTM C 618) with varying AEA demand, based on prior laboratory experience. In this study, fly ashes 6 and 7 were obtained from a coal fired power plant utilizing a Low NOx burner technology. No information was obtained about the coal type, chemistry or burning conditions. Both of these fly ashes have a high AEA demand in concrete despite having a low LOI (less than 0.8%). In order to reduce the AEA demand, fly ash 6 was treated with a commercially used sacrificial surfactant (Hill, et al. 2004) that has been suggested to improve the AEA demand in concrete by preferentially absorbing on the carbon in the fly ash. No information was provided by the manufacturer about the amount or specific chemical nature of the sacrificial surfactant that was added

to the fly ash. Therefore, all results for fly ash 6 are likely dependent on the amount and chemical nature of this additive. Oxide analyses completed with x-ray fluorescence spectroscopy and loss-on-ignition (LOI) measurements from ASTM C 311 are reported in Table 5.2 for each fly ash.

5.2.2 Mixture Preparation

All of the mixtures presented in this chapter contained a river gravel aggregate, with the exception of two mixtures that were used to analyze the aggregate correction factor and hence contained a limestone aggregate with a higher aggregate correction factor. The mixture proportions for these are shown in Table 5.3. In all cases the mixtures were prepared by the following method. A 64-L batch of concrete was made in a 85-L drum mixer. All of the material for the mixture was stored in the mixing room for at least 24 hours at 23^{o} C prior to mixing to keep the mixing temperature constant. Coarse and fine aggregates were brought in from the stock piles and individually mixed. A moisture correction for each was used to adjust the batch weights. The coarse aggregate and sand were added to the mixture first and then 2/3 of the mixing water was added. The mixture was agitated for one minute. Next the cement, fly ash and the remaining mixing water were added and mixed for three minutes. At this point the mixer was stopped and any material gathering on the sides or back of the mixer was removed. During the final three minute mixing period the mixture was brought to a constant slump (ASTM C 143) of 87.5 mm +/- 37.5 mm using a water reducer. Due to water demand differences of the fly ash mixtures the dosage of the WR and MWR varied. It is expected that different results would be obtained with the same materials when mixed for different durations, at different mixing speeds, or with different mixing energy per unit volume of mixture. Nevertheless, this method allowed for useful comparisons of the variables investigated.

5.2.3 Determining Aggregate Correction Factors

As mentioned previously, ASTM C 231 specifies a method to determine the impact that an aggregate has on the air content of a mixture. In this method an equivalent amount of coarse and fine aggregate is used in the moisture condition that matches the material that is to be used in the concrete mixture. This material and water are then added to the pressure meter chamber and the mixture is stirred and consolidated in order to remove any trapped air voids. After the chamber has been filled to capacity then a certain volume of water is removed from the slurry equal to the volume of air for which the mixture is designed.

ASTM C 231 states that the aggregate correction values are not directly related to the absorption capacity of the rock. However, limited results in this study showed that the aggregate with a higher absorption capacity also showed an increased aggregate correction factor. The aggregate correction values for the mixtures utilizing the river gravel and natural sand and the limestone and natural sand were found to be 0.55% and 1.75%, respectively. The aggregate correction was not applied to the data reported for the pressure meter analysis as one goal of this testing is to best replicate the field application of the test method. However, all but two of the mixtures investigated were prepared with river gravel aggregate and so the correction factor is low. The aggregate correction factors for the aggregates used in the study are shown in Table 5.4 with various moisture contents investigated at a 5% air content. Each value is an average of two measurements. All measurements were completed with either just the coarse or fine aggregate so that the individual contribution of each material could be investigated.

5.2.4 Hardened Air-Void Analysis

All of the hardened air-void analysis was completed in this study by using an automated air-void analysis with the RapidAir 457 instrument (Concrete Experts International). In order for samples to be analyzed in this machine the surface of the sample is prepared according ASTM C 457 and then painted black. Next a fine white

powder (< 1 μm) is added to the samples surface and forced into the voids. This technique is described in EN 480-11. After the extra powder is removed from the surface any voids that are found inside the aggregate that became filled with powder must be painted black. The machine uses the contrast between the surface of the sample and the powder contained in the voids to measure the air-void chord lengths with a linear traverse measurement technique. This analysis technique is not able to measure the paste content of the sample as the machine can not distinguish the difference from the paste and aggregate. Therefore, this information is required to be input from the mixture proportions or a manual modified point count method. For this study this value was obtained from the mixture proportions and fresh air content. The results of the hardened air-void analysis are not able to be classified as meeting the specifications of ASTM C 457 as the test requires the analysis to be completed by a human. Because of this, the results for the test will be referred to as the "hardened air-void analysis" in the remainder of the document. Several publications have shown outstanding repeatability of measurement and a good correlation between the analysis determined by the automated system and ASTM C 457 linear traverse (Pade et al., 2002, Jakobsen et al., 2006).

All of the samples presented in this study were analyzed by utilizing a traverse length of 7240 mm over an area of 77 cm^2. This is equal to a length 3.17 times larger and an area of 1.08 times larger than is required in a traditional ASTM C 457 analysis with a maximum nominal aggregate size of 19 mm. Because of the larger traverse length that was utilized the analysis should provide a more thorough investigation of the air-void system of the sample. While a precision statement was not prepared for the use of the hardened air-void analysis as utilized in this paper, data by Pleau et al. (1990) suggests that when three analyses are completed on a sample that the maximum error decreases from 20% to 12% for the spacing factor, 24% to 15% for the specific surface, and 27% to 16% for the total air content measured. While these precision values were not

determined for this analysis technique one would expect a similar decrease in maximum error as the length of analysis increased.

The RapidAir 457 requires that the user choose a threshold value for the sample. This portion of the analysis is somewhat subjective. There is little guidance provided by the documentation or training with the RapidAir 457 to guide a user on how to accurately choose a threshold value for a sample. However, it has been shown with a limited data set that the threshold value chosen does not have a large impact on the results of the analysis as long as a consistent method is utilized to evaluate the appropriate value for the specimen (Appendix A). All of the threshold values for the specimens in this study were between 158 and 174.

For the results of the hardened air-void analysis reported in this chapter the chords smaller then 30 μm were not included in the analysis as they are not able to be detected by a human during the ASTM C 457. By excluding these chords the air-void parameters determined by the hardened air-void analysis are better comparable to other reported values of ASTM C 457 results.

5.3 RESULTS

5.3.1 AVA

To examine the repeatability and comparison between the results obtained in the AVA and the hardened air-void analysis ten different mixtures were examined with fresh air contents from 3.2% up to 9.75%. For five of these mixtures two samples were taken from each mixture and the results compared to one another. Table 5.5 provides a summary of the maximum, minimum and average standard deviations between each one of the measurements. The average percent differences between each AVA measurements for the air content, specific surface, and spacing factor were 36%, 48%, and 36%, respectively.

In Table 5.6, results are presented for the analysis of ASTM C 231 fresh air content (pressure method), hardened air content, and the AVA. Testing was completed with four different fly ashes and four different AEAs. If more than one sample was taken from a mixture then the average results were reported. Note that the air content reported by the AVA is only for bubbles with diameters less than 3 mm. Because of this, the air content of the hardened air-void analysis was also only reported for voids less than 3 mm in size. The average percent differences between the AVA and hardened air-void analysis for the air content, specific surface, and spacing factor are 56%, 30%, and 63%, respectively.

5.3.2 Impact of Mixture Ingredients on an Air-Void System

Figure 1 shows a comparison between the hardened air content and the results of the pressure meter for 39 different mixtures that contained 7 different fly ashes, 5 different AEAs, and two different coarse aggregate. The line of equality between the two is shown as well as a linear trend line. The average difference between the hardened air void analysis and the pressure meter was found to be 0.19% with a standard deviation of 1.18%.

In order to assess the freeze thaw durability of mixtures between 3% and 5% of fresh air content as determined by ASTM C 231, a hardened air-void and ASTM C 666 analysis were completed to determine how certain parameters affect the performance in the rapid freeze-thaw test and the air-void parameters. A summary of the data is shown in Table 5.7.

5.4 DISCUSSION

5.4.1 AVA

No previous data has been published indicating the repeatability of measurement for the values of the specific surface and air content reported by the AVA from a single

mixture analyzed multiple times by the same machine. There has been work published by Distlehorst and Kurgan (2006) about the repeatability of the spacing factor. This work suggested that the single operator variance using the same machine is not expected to be more than 43%. The average difference between values of 36% obtained in this study is within this range for the spacing factor and so the variance of the other two parameters is likely characteristic of measurements taken by the AVA. The variance of measurement between devices has been suggested to be significant enough that the use of the AVA has not been recommended to be implemented in a construction specification (Desai et al., 2006).

When one compares the results between the estimates of the hardened air-void analysis and AVA shown in Table 5.6 the difference between the results is quite variable. The results between the two methods for the air content, specific surface and spacing factor show little agreement. The air content reported in the AVA and the hardened air-void analysis were on average different by more than 50%. In only three cases out of ten was the air content within 1%. The parameter that showed the closest correlation to the hardened air-void analysis was the specific surface measurement at an average difference of 30%. It is encouraging that this parameter shows the closest correlation as it is the one most directly calculated from the measurements of the AVA.

Thus, the overall findings of this study show that the AVA showed poor repeatability and that the estimated air-void parameters measured did not correlate well to air-void parameters estimated by the hardened air-void analysis from the same mixtures.

5.4.2 Impact of Mixture Ingredients on an Air-Void System

Figure 5.1 shows a comparison between the air content measured by ASTM C 231 and the hardened air-void analysis is shown in Fig. 5.1. This figure shows a good correlation between the two methods; however, one should keep in mind that both of these tests can have significant variance. It should also be noted that the vast majority of the samples analyzed contained air contents less then 6%.

Although the data in Table 5.7 allow for many different trends to be investigated, the discussion in this chapter will focus on the impact of different mixture ingredients on the quality of the air-void parameters and performance in the ASTM C 666 with air contents between 3.2 and 5% as measured by ASTM C 231. These ranges of air contents were chosen as they allow the performance of mixtures with different ingredients to be investigated at the low end of specified air contents (as described earlier in this chapter). Some of the variables investigated include: different aggregate correction factors, impact of WR dosage on the air-void system, and the impact of a high AEA demand fly ash that has been treated with a sacrificial surfactant to improve the AEA demand. Each variable was investigated with a range of air contents in order to find the threshold value of fresh air content that was needed to provide a performance in the ASTM C 666 test similar to the requirements specified in ASTM C 260, ASTM C 494, and ASTM C 1017. It was decided that a durability factor of 75 would be used as the point of failure for the testing in this study.

5.4.3 Aggregate Correction Factor

As can be seen in Table 5.4, the aggregate correction factor seems to be dependent not only on the aggregate porosity but also on the moisture content. Therefore, the difference between the air content in the matrix and the amount reported by the pressure meter for the limestone aggregate mixtures is significantly different and will vary based on the moisture condition of the aggregate during the test. This may lead to a situation where an operator that is only investigating the air content of a mixture with the ASTM C 231 method to determine that the mixture has a large enough volume of air to provide satisfactory freeze-thaw performance when it does not. An example of this can be seen if one compares the results from specimens 2 and 10 in Table 5.7. The aggregate correction factor for specimens 10 and 11 was determined to be 1.75% while the aggregate correction factor for the remainder of the mixtures was 0.55%. In both of these specimens a similar air content was determined by fresh air content analysis of

4.5% and 4.2% by ASTM C 231 with no aggregate corrections applied; very different air content results when the aggregate correction factor is applied of 3.95% and 2.45%. It seems that this amount of air was not enough in mixture 10 as a durability factor of 75 was obtained in the rapid freeze-thaw tests, while specimen 2 had a durability factor of 90. In specimen 11 the AEA dosage was increased, which corresponded to an increase in the corrected air content to be 3.25% which exhibited an improvement of the air-void parameters and performance in the ASTM C 666 test. However if one does not apply the aggregate correction factor then an air content of 5% in the ASTM C 231 test was needed to ensure adequate performance in the ASTM C 666 test with the limestone aggregate mixture, while the 3.3% air content in specimen 1 was enough to ensure satisfactory performance. It is unclear how differences between mixtures of the w/cm, type of WR, and paste content may have affected the results of the ASTM C 666 tests. However, these data do suggest that the use of a high porosity aggregate can lead to unsatisfactory frost performance in the ASTM C 666 test with air contents less than 4.2% as measured with by ASTM C 231 if the aggregate correction factor is not applied.

5.4.4 Impact of WR Dosage

The impact of WR dosage has been shown to improve the effectiveness of an AEA to produce a larger volume of air in a concrete mixture for a similar dosage (chapter 4). In this study the impact on the hardened air-void system and performance of the mixtures in the rapid freezing and thawing tests is examined. In specimens 3, 4, and 5 the amount of AEA and WR was varied in each mixture containing a fly ash with a high AEA demand, due to high activity carbon to examine the impact on the hardened air-void analysis, and the performance in the rapid freeze-thaw test.

Between specimens 3 and 4 the dosage of AEA was held constant while the WR dosage was 180% larger in specimen 4. With this increase in WR dosage the air content measured in the ASTM C 231 test increased and an improvement was obtained in the specific surface. However the spacing factor did not change. Furthermore, both

specimens performed adequately in the ASTM C 666 test. In specimen 5 a WR dosage was used that was 380% larger and an AEA dosage that was 59% less then what was used in specimen 3. The air-void content and distribution measured was very different despite a similar air content measured by ASTM C 231. The performance in the rapid freeze thaw test was also different as specimen 5 showed very poor performance in the ASTM C 666 test. Furthermore, if one looks at the difference between the hardened air content and that measured by ASTM C 231 for specimen 4 and 5 it can be seen that the amount of air in the hardened concrete has decreased between the fresh and hardened state. This decrease in air content implies that there may be an air-void stability problem in concrete with high dosages of WR. This observation is in line with results reported by Plante et al. (1989) where mixtures with large dosages of WR when compared to AEA showed a decrease in air content with time. These data along with the 36 mixtures provided by Plante et al. (1989) suggest that a WR is capable of increasing the measurement of air content in the fresh concrete above levels that would be produced with an AEA alone and yet produce unsatisfactory performance in ASTM C 666 test.

5.4.5 High Activity Carbon Fly Ash Treated with a Sacrificial Surfactant

As stated previously a sacrificial surfactant has been used to reduce the AEA demand of fly ash 6 in concrete. This fly ash was investigated with three different AEAs as shown in Table 5.7. In each case a range of air contents was investigated and it was common to find that higher total air volumes were needed in the fresh and hardened air content for fly ash 6 before the durability factor determined by the ASTM C 666 was above 75 when compared to mixtures that did not contain a sacrificial surfactant. The spacing factors and specific surfaces as determined by the hardened air-void analysis were not sufficient to satisfy the recommended values of 0.200 mm and 24 mm^2/mm^3 and yet satisfactory durability factors were obtained in the ASTM C 666 test. One other observation is that all mixtures containing fly ash 6 with a hardened air content greater than or equal to 5% showed satisfactory performance in the ASTM C 666 for all AEAs

used. These data imply that the use of a sacrificial surfactant may cause an increase in the air-void sizes produced in air-entrained concrete and therefore, a larger volume of air was needed in the mixture to obtain a satisfactory number of small air-voids and performance in the ASTM C 666 test. This difference in void size can be clearly seen when one compares the average chord lengths of specimens 1, 3, 4, and 7 or 12 and 14.

This behavior is especially clear when one compares specimen 4 with specimen 7. The fly ash in specimen 4 is the same as used in specimen 7 except for the sacrificial surfactant. In both mixtures all other parameters were held the same except for the AEA dosage and the air content. Specimen 4 is shown to have a satisfactory durability rating with a hardened air content of 2.48% and specimen 7 did not show a satisfactory durability rating with an air content of 3.70%. As stated previously the reason for the difference in behavior is that specimen 7 appears to have a coarser air-void system. This can be seen directly when one compares the average chord lengths, specific surface, and spacing factor between the two samples. The average chord length suggests an increase of 39% between the two samples. Despite this apparent coarsening of the air-void system, when sufficient air was entrained in these mixtures (5% or more), satisfactory frost resistance was obtained.

5.5 CONCLUSIONS

This work presented in this chapter examined the challenges of relying on a fresh air-void specification to determine the ability of a mixture to provide satisfactory freeze thaw resistance in the ASTM C 666 test. An evaluation of the AVA was presented that investigated the repeatability of measurement with the device and also the difference in values compared the hardened air-void analysis with the RapidAir 457. Although the results of this testing are based on a small number of mixtures that had a similar workability and mixture proportions the results obtained suggested that the AVA has significant variability between two measurements examined from the same mixture, and significant differences were found between air-void parameters estimated by the

hardened air-void analysis and the AVA. More work is needed to determine the causes of these discrepancies; however, the variability between the two measurements from the same mixture was similar to values obtained by Distlehorst and Kurgan (2006), and significant discrepancies between the hardened air-void analysis and the AVA measurements were also observed by Desai et al. (2006) and Magura (1996).

One of the primary concerns of the authors with the AVA is the ability to obtain a meaningful representation of a concrete mixture from a 20 cm^3 sample. Furthermore, the version of the AVA investigated utilized a balance that was only accurate to 0.01 g. It is unclear if this is precise enough to measure the buoyancy change in the Petri dish as it collects air bubbles.

Several concrete mixtures with relatively low total air contents were evaluated, and it was shown that concrete with a total air content greater than or equal to 5% was generally frost resistant. Some mixtures with lower air contents were not frost resistant (using ASTM C 666), especially mixtures containing high amounts of WR (and lower AEA dosages), mixtures for which aggregate correction factors were not applied, or mixtures containing a fly ash treated with a sacrificial surfactant. However, none of these variables listed previously were investigated in combination; combinations of these variables could require a larger volume of air to be contained in the mixture.

For mixtures containing a fly ash treated with a sacrificial surfactant, a coarsening of the air-void system was observed when compared to mixtures prepared with similar types of AEA and volume of air. This coarsening was directly observed as an increase in the average chord length of air voids, increase in the spacing factor and decrease in the specific surface. However, once the air content was increased to 5% or more, satisfactory frost resistance was obtained. It should be stated that no details were provided nor were they obtained about the concentration or chemical nature of the sacrificial surfactant. If either one of these parameters change then the results may also change.

Table 5.1 – Composition of the Type I/II cement as obtained through RQRXD

phase	percentage
C_3S	68.0
C_2S	15.7
C_3A	2.7
C_4AF	8.7
gypsum	1.3
$CaCO_3$	2.6

Table 5.2 – Oxide analysis and LOI data for three fly ashes

Fly Ash Name	1	6	7
Silicon Dioxide (SiO_2), %	56.18	52.07	52.04
Aluminum Oxide (Al_2O_3), %	20.37	23.65	23.75
Iron Oxide (Fe_2O_3), %	6.77	4.55	4.59
Sum of SiO_2, Al_2O_3, Fe_2O_3, %	83.32	80.27	80.38
Calcium Oxide (CaO), %	9.95	12.76	12.63
Magnesium Oxide (MgO), %	2.55	2.02	2.01
Sulfur Trioxide (SO_3), %	0.53	0.78	0.79
Sodium Oxide (Na_2O), %	0.47	0.31	0.28
Potassium Oxide (K_2O), %	1.08	0.80	0.81
Total Alkalies (as Na_2O), %	1.18	0.84	0.81
ASTM C 618 Classification	F	F	F
LOI (ASTM C 311)	0.12	0.79	0.79

Table 5.3 – Concrete Mixture Composition

Components	Mass (kg/m^3)	
Cement	268	208
Fly Ash	67	89
Coarse Agg.	1098	1075
Fine Agg.	742	772
Water	151	113
total cm	335	297
Coarse Aggregate Type	River Gravel	Limestone
Agg. Correction Factor	0.55%	1.75%
w/cm	0.45	0.38

Table 5.4 –Aggregate correction factor for three aggregate sources with various moisture content.

aggregate description		moisture content (%)	percent saturated (%)	ASTM C 231 correction factor (%)
river gravel	oven dry	1	0	0.4
	stock pile	0.68	68	0.3
	SSD	0	100	0.1
limestone	oven dry	4.5	0	1.8
	stock pile	2.5	56	1.5
	SSD	0	100	1
natural sand	stock pile	1.02	59	0.25

Table 5.5 –Repeatability of five different mixtures each analyzed twice with the AVA

	air content (%)	specific surface (mm^2/mm^3)	spacing factor (mm)
maximum difference	2	29	0.092
minimum difference	0.50	7.6	0.030
average percent difference	36	48	36

Table 5.6- Comparison of estimates from the pressure meter, hardened air-void analysis and the air void analyzer.

ASTM C 231 pressure meter	hardened air-void analysis			AVA		
air content (%)	air content* (%)	specific surface (mm^2/mm^3)	spacing factor (mm)	air content* (%)	specific surface (mm^2/mm^3)	spacing factor (mm)
3.2	3.66	24.81	0.209	4.2	35.2	0.143
4.2	3.27	23.37	0.232	2.75	30.4	0.198
4.5	5.61	17.16	0.240	6.05	32.4	0.14
5.7	6.98	25.92	0.127	2.3	22.6	0.280
6.0	3.83	23.24	0.216	2.05	21.0	0.329
6.1	5.73	23.12	0.172	3.5	16.3	0.319
6.4	6.08	24.99	0.149	2.6	16.3	0.368
8.5	9.99	27.54	0.081	3.7	18.4	0.293
9.0	7.66	29.46	0.098	4.3	22.1	0.213
9.75	11.47	30.63	0.062	4.7	34.4	0.131

* The air content only includes voids that are less than 3 mm in size.

Table 5.7 – Comparison of mixture information, fresh air volume, hardened air-void analysis, and rapid freeze-thaw testing.

specimen	fly ash	AEA type	AEA dosage (mL/100 kg cm)	WR/MWR dosage (mL/100 kg cm)	ASTM C 231 air content (no correction) (%)	ASTM C 231 air content (w/ correction) (%)	hardened air-void analysis: air content (%)	specific surface (mm^2/mm^3)	spacing factor (mm)	void freq. (mm^{-1})	avg. chord (mm)	ASTM C 666 durability factor	ASTM C 666 standard deviation
1	1	wood rosin	18	44	3.3	2.8	3.31	26.72	0.203	0.221	0.150	93	5.2
2	1		21	98	4.5	4.0						90	4.9
3	7		87	46	3.7	3.2	3.31	20.30	0.266	0.168	0.197	94	0.2
4	7		83	83	4.5	4.0	2.48	26.68	0.233	0.165	0.150	93	2.1
5	7		36	177	4.0	3.5	2.73	17.64	0.336	0.121	0.227	16	0.0
6	6		32	108	3.2	2.7						18	9.9
7	6		32	90	3.6	3.1	3.70	17.85	0.288	0.165	0.222	40	10.7
8	6		61	110	4.0	3.5	4.16	19.10	0.254	0.199	0.209	67	1.2
9	6		95	105	5.0	4.5	5.22	20.45	0.214	0.267	0.196	94	2.4
10*	1		8	111	4.2	2.5	3.27	23.37	0.232	0.191	0.171	75	4.2
11*	1		15	136	5.0	3.3	4.46	18.69	0.225	0.255	0.214	96	0.7
12	1	Vinsol resin	9	33	4.0	3.5	4.68	23.65	0.196	0.277	0.169	93	0.1
13	6		41	34	3.2	2.7	4.33	18.44	0.260	0.200	0.217	26	3.5
14	6		66	33	3.9	3.4	4.71	19.71	0.234	0.232	0.203	62	0.6
15	6		124	32	4.5	4.0	5.61	17.16	0.240	0.241	0.233	93	1.4
16	6	synthetic	23	33	3.2	2.7	2.99	16.28	0.350	0.122	0.246	18	8.5
17	6		27	33	3.9	3.4	5.59	19.65	0.211	0.275	0.204	91	1.6

These mixtures contain limestone coarse and natural sand fine aggregate with an aggregate correction factor of 1.75%.
The other mixtures contain a river gravel coarse and natural sand fine aggregate with an aggregate correction factor of 0.55%.

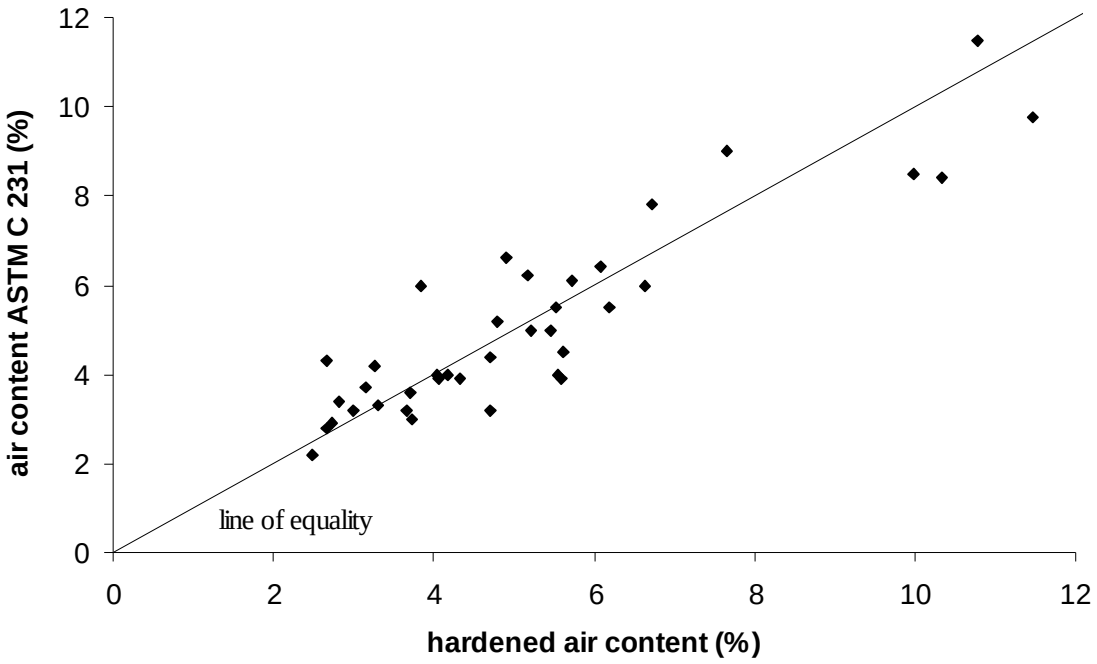


Fig. 5.1 – Comparison of air content from the ASTM C 231 pressure method and the hardened air content

Chapter 6: Observations of Air-Bubbles from Fresh Cement Paste

Abstract

Recent experimental work is also presented using a new technique to observe bubbles that have escaped from pastes and suspended in the bleed water. These experiments suggest that the stability of an air-entrained bubble may be related to the integrity of this shell. This paper also reviews literature dealing with changes to air bubbles with time in fresh air entrained cement paste and concrete. Coverage is also given to the existence of a shell surrounding these bubbles.

6.1 INTRODUCTION

Development of an air void system in hardened concrete through the use of an air entraining admixture (AEA) to stabilize air bubbles in fresh concrete is the primary method of producing freeze-thaw-resistant concrete. Although AEAs are widely specified and used to obtain frost and salt scaling resistance, practitioners still face significant problems in reliably and reproducibly stabilizing and maintaining an effective air-void system in concrete. Existing literature, based on laboratory and field observations, suggests that all aspects of the concrete construction process can affect the air void system in concrete (Whiting and Stark, 1983). In addition to the influence of dynamic processes such as batching, mixing, transporting, placing, consolidating and finishing the concrete, it has been reported that air bubbles in fresh concrete can change while the plastic material is at rest (Mielenz et al., 1958; Fagerlund, 1990). The purpose of this paper is to report several experimental observations of air bubbles that have escaped from cement paste and observed over time.

The goal of this paper is to resolve some of the conflicts presented in previous research. This was achieved by developing a new experimental method that uses

microscopy to examine the changes in bubbles separated from 0.42 w/cm paste. While these observations are not numerous enough to obtain an understanding of the behavior, they do provide insight. Follow up testing is planned to examine the air-void stability of concrete.

6.1.1 Background

While there has been a large amount of research completed on the bulk properties of air-entrained concrete there has not been a large amount of work done to fundamentally investigate the air-voids themselves or how they change with time. One classic and frequently cited collection on air-entrained concrete is the series of four papers by researchers at the U.S. Bureau of Reclamation (Mielenz et al., 1958A, Backstrom et al., 1958A; Backstrom et al., 1958B; Mielenz et al., 1958B). The first (Mielenz et al., 1958A) of these papers included data suggesting that due to a pressure gradient between large and small bubbles, gas transfer can occur between bubbles. This transfer leads to a change in volume of the air entrained in pastes with time. Photos of air-entrained bubbles in dilute water-to-cementitious materials ratio (w/cm) pastes were also shown to change while sitting statically. Bruere (1962) attempted to replicate some of the behavior previously described by Mielenz et al. (1958A) with a different experimental setup, and found no air bubble instability. In a review of both sets of experiments Powers (1968) states that it is doubtful that bubbles will be able to expand in fresh cement paste because of the restraint provided by the cement paste. Other researchers identified a “transition zone” around bubbles that had been frozen during the first 3 hours of hydration and observed cryogenically with a low temperature scanning electron microscope (LTSEM) (Ahmad and Williamson, 1991A, 1991B; Corr et al., 2002). This transition zone was suggested to be filled with water (Ahmad and Williamson, 1991A) or of a phase with a high porosity (Corr et al., 2002). The size of the transition zone was suggested to increase with an increase in w/cm and shrink with hydration. A summary of previous work is provided in Table 6.1.

6.2 EXPERIMENTAL METHODS

To augment the studies described above, an experimental program was initiated to observe in-situ changes in air bubbles that had escaped from cement pastes, and were monitored over time as the bubbles resided in a static bleed-water solution. For this testing, a 0.42 w/cm paste was made using 1.37 kg of a cement meeting the ASTM C 150 specifications for Type I and II with a 0.53 alkali content (Na_2Oeq). Table 6.2 presents a summary of the admixture combinations investigated. The mixer and mixing procedure used in this study met ASTM C 305. After the mixing cycle was completed, a funnel was used to transfer the paste into a 70 ml bottle that was filled in thirds by volume and consolidated by agitation and taping on the desktop. Care was taken to ensure the bottle did not have any large air-voids and was filled until it reached capacity. At this point the cap was tightened and the bottle was turned on its side. After about 10 minutes it was possible to observe a layer of bleed water forming at the surface of the paste. In this bleed water air bubbles could be found that had worked their way to the inside face of the bottle wall due to buoyancy. These bubbles were then observed under a stereo microscope at magnification of 50X, fitted with a 5 megapixel, high resolution digital camera. A computer program was written to capture images of the changes in these bubbles with time. These images were measured with the AxioVison AC software from Carl Zeiss. This software allows the user to count pixels between any two designated locations on the image and converts pixels to units of length via an image-specific calibration. Accuracy of the measuring system had been checked and calibrated by the instrument manufacturer. When objects of fixed size were subsequently measured twenty times the software reported coefficients of variation ranging from 0.3% for lengths of 700 microns to 1.3% for lengths of 30 microns. For bubbles sizes reported in this paper a

representative coefficient of variation (COV) is about 0.4%, including any effects of distortion by the plastic bubble wall.

6.2.1 Setup #1

Setup #1 is shown in Fig. 6.1. In preliminary tests it was found that the paste in the bottle swelled as hydration progressed. Since the bottle was filled to capacity the change in volume of the paste disturbed the voids that had escaped the paste and these were then caught on the surface of the bottle in the bleed water. The swelling of the paste was likely related to temperature increase (due in part, perhaps to heat of hydration, and in part to a high-intensity light source), as swelling of the paste was no longer observed once the sample was maintained in isothermal conditions. (A plot of the average temperature from two thermocouples in the ambient room, in a specimen under the point light source, and in a specimen in the ambient temperature is shown in Fig. 6.2. These measurements were taken on two different occasions and the results did not vary by more than 1^{o} C between the measuring periods. The average temperature changes with time for the different specimens can be found in Fig. 6.2.) While this swelling was unexpected it proved to be useful as the bubbles could be inspected as they were pushed by the paste from below.

In order to monitor the upwards movement of the paste as it swelled, with respect to the air-bubbles, a single point light source was used at a sharp angle so that the shadow of the bubble could be monitored with time. Since the bubble was stationary at the underside of the bottle wall, an apparent movement of the shadow towards the bubble means that the surface of the paste is moving upwards.

6.2.2 Setup #2

In order to isolate the changes in the bubbles without contact from the paste an alternate setup was used. The only difference in this test setup from the previous is that the bottle of paste was filled to 75% of capacity and the balance of the volume kept full

of a surrogate bleed water solution by means of a tube connected to the cap as shown in Fig. 6.3. The surrogate pore or bleed water solution (water and cement at w/cm = 60) was carefully added so that it filled the remaining portion of the bottle and the tube, and minimized mixing with the paste in the process. Some agitation was needed to remove air bubbles trapped during filling with the bleed water solution, accomplished by flicking the tube of the bottle with a finger. After this solution was added the bottle was carefully turned on its side and the paste formed a slope as shown in Fig. 6.3. After 10 minutes in this position air bubbles were seen to escape from the 0.42 w/cm paste, and floated up to the underside of the bottle. Changes in the bubbles were then observed with time as previously described. Because the bottle was not filled to capacity, once it was put on its side the bleed-water filled gap isolated the bubbles from contact with the paste, and allowed this migration to the underside of the glass surface. This ensured that any changes in bubble diameter with time were solely due to interactions between the bubbles and the surrounding fluid in combination with any effects of temperature-changes in the air within the bubbles.

6.2.3 Setup #3

A final setup was used to investigate the effect of pressure on escaped air bubbles from cement paste. While additional work is underway in this area, these test results were included because the stability of static air-bubbles as the surrounding fluid pressure is influenced by concrete placing methods, consolidation, and by the static head of the fresh concrete. For this test the fluid surrounding the air-bubbles was increased to 0.7 bar above atmospheric pressure in 10 equally-spaced steps and then decreased back to atmospheric pressure in three equal steps. It should be noted that the pressure regime was chosen based on limitations of the available equipment.

6.3 RESULTS AND DISCUSSION

6.3.1 Results of Setup #1-paste expansion

6.3.1.1 Air bubbles from Air-Entrained Cement Paste

The images of escaped air bubbles from an air-entrained cement paste with a tall oil AEA as per mixture 1 in Table 6.2 (per setup #1) are shown in Fig. 6.4. These experiments have been completed 3 times with a Vinsol resin, wood rosin, and synthetic AEA at dosages typical of air entrained concrete, and similar behavior was observed for all. A summary of experiments is shown in Table 6.2. These images were chosen as they are a representative set that clearly shows the behavior. The bubbles in Fig. 6.4 appear to have a textured surface similar to that observed by Mielenz, et al. (1958A) and Corr (2002). If one compares Fig. 6.3A and 6.3B the shadow of the air-voids from the point light source has moved towards the bubble with time. The point of focus of the microscope was never changed and the bubbles have remained in focus the entire time; therefore, the depth between the bottle surface and the bubble did not change beyond the depth of focus, which for this instrument at this magnification is about 1 mm. As shown previously in Fig. 6.1 this is only possible if the paste is expanding towards the bottle surface. Once the paste swells enough to touch the bubble, the shell appears to crack in a brittle manner. As the paste swells further one can see a much smaller bubble that appears to emerge from the inside of the cracked shell. This emerging bubble seems to have a different, much smoother surface than the shell that was previously observed. As the paste continues to swell and the bubbles are forced to interact no coalescence is observed as the bubbles touch one another (6.4D and 6.4E). In Fig. 6.4E one can see that as bubble B and A come into contact with each other the surface of bubble B appears to have curved away from the surface of bubble A. As further paste expansion occurs in Fig. 6.4F bubble A appears to have surrounded bubble B without coalescence.

6.3.1.2 Air bubbles from Non-Air-Entrained Cement Paste

The images from a non air-entrained cement paste observed in test setup #1 are shown in Fig. 6.5. The bubbles in this system appear to be translucent-to-transparent and do not have the rough or opaque surface texture previously observed with bubbles escaped from air-entrained paste. Again the shadows of the bubbles from the point light source move closer to the bubble with time while the bubble is stationary, and so again the paste appears to be rising upwards. Once the paste contacts the bubble, one can see that the bubble diameter begins to expand without an apparent change in the bubble surface. As paste expansion and the accompanying bubble deformation continues, Fig. 6.5E shows that once bubbles C and D come into contact they coalesce and form a larger void. This behavior contrasts with that observed in the previous experiment in which bubbles that escaped from air-entrained paste appeared to resist coalescence. Several dimensions are given for bubble C in Fig. 6.5A, 6.5B, and 6.5C showing that this bubble did change diameter with time before it came into contact with the expanding paste (as indicated by the shadow technique described earlier.) This is discussed further in Setup #2. This test was repeated three times with similar behavior each time.

6.3.2 Results of Setup #2-no paste expansion

6.3.2.1 Bubbles from Air-Entrained Cement Paste

When air-entrained cement paste was tested in this setup, there was no measurable change in the diameters of the bubbles that had escaped into the fluid above the paste over the 8- hour period of observation. This test was repeated four times with a similar size distribution of observed bubbles and little to no diameter change was observed for the following AEAs investigated: tall oil, Vinsol resin, wood rosin, or so-called “synthetic” as reported in Table 6.2.

6.3.2.2 Bubbles from Non Air-Entrained Cement Paste

When bubbles from non air-entrained cement paste were examined over time in setup #2, it was found that there was a significant change in bubble diameter for the first 3.5 hours after hydration. A picture of the layout of the bubbles is shown in Fig. 6.6 at 0.6 and 3.6 hours of hydration, and the same translucent-to-transparent bubble walls are evident as seen earlier when the bubbles originated in non air-entrained paste. A graph summarizing the average change in diameter with time is shown in Fig. 6.7. For the diameters reported in Fig. 6.7, two measurements were taken that were perpendicular to one another and then averaged. As can be seen bubble "I" begins to decrease in size from the initial observation until about 1 hour of hydration. Bubbles "M" and "K" begin to decrease in size at about 2 hours after initial hydration and stabilize after about 3 hours. Bubbles "J" and "L" begin to increase in size from the initial observation and stabilize at 2 hours of hydration. The smaller bubbles appear to decrease in size initially while the larger bubbles appear to increase in size. The mid-sized bubbles remain a constant diameter initially, and then start to decrease in size. A proposed explanation for the size change of different diameter voids has been suggested by Fagerlund (1990), who hypothesized that the smallest (higher-pressure) bubbles lose air to the largest (lower pressure) bubbles while intermediate sized bubbles would show no volume change. (Thus all bubbles in the system tend towards an equilibrium pressure and size). Fagerlund went on to propose that the bubble-size distribution would continuously change until such an equilibrium is reached. The observations of this present experiment not only support Fagerlund's ideas, but are also similar to the observations by Mielenz et al. (1958A) for air-entrained paste with a w/cm of 30. The experiments reported here were repeated 4 times and each time many, but not all, of the smaller bubbles decreased in size over time while the larger bubbles increased in size.

6.3.3 Setup #3-Varying Fluid Pressure

6.3.3.1 Response of an Air Bubbles to Pressure

In Fig. 8A an approximately 400 μm diameter bubble from mixture 6 is shown at atmospheric pressure. One first notices that the bubble shell with the Vinsol Resin and water reducer used here appears to be different from the shell observed in Figure 4, which had been stabilized with a tall oil AEA and no water reducer. This difference is stark and is likely to be important, but is beyond the scope of this paper. Further, in Fig. 6.8A through 6.8D the fluid pressure around the bubble is being increased. In Fig. 6.8D one can see that the air bubble has decreased in diameter such that bubble volume at 0.7 bar overpressure is 58% of the volume of the same bubble at 0 bar overpressure. Since simple application of Boyle's Law would have predicted 59%, it appears that this particular bubble is behaving as an elastic, gas-filled body with no significant surface tension effects. (The degree to which this finding can be generalized to other bubble sizes, stabilized with other AEA's deserves further investigation, some of which is already in progress.) Further, it is interesting to note that the shell around the bubble does not appear to be distressed by the significant decrease in diameter during the pressurization phase. In Figs. 6.8E and 6.8F the fluid pressure is reduced to atmospheric pressure. As this is taking place one can see in Fig. 6.8E that the shell of the large air bubble cracks as the bubble is increasing in volume during the depressurization phase. These cracks widen in Fig. 6.8F as the fluid returns to atmospheric pressure. It can be seen that the void is no longer covered by the shell. Furthermore, it appears that some air contained in the bubble has been lost to the surrounding fluid during the overall pressure cycle as the final diameter does not match the initial diameter (net reduction in diameter of 6%, which would correspond to about a 17% reduction in air volume if the internal pressure was the same before and after the pressure cycle was applied). This experiment has been repeated over 10 times with Vinsol resin and wood rosin AEAs at dosages shown in Table 6.2 and each time many but not all bubbles with diameter of 200 μm or

greater were observed to crack while the pressure was decreased. (These images were chosen for their clarity.) From observations at this magnification it is difficult to observe if the shells of smaller bubbles are also damaged upon depressurization.

6.3.3.2 Changes in a Bubble with Time After the Shell Has Been Damaged

Pictures in Fig. 6.9 show the changes in a collection of bubbles stabilized with a wood rosin AEA from mixture 4 over approximately three hours after being subjected to a pressure of 0.7 bar and returned to atmospheric pressure. The pictures in Fig. 6.9 show the changes in the collection of bubbles at the conclusion of pressure cycle. As can be seen the shell of the bubble labeled P in Fig. 6.9 has been damaged during the depressurization phase and appears to be "shedded" by the bubble over time. Also the smaller bubbles N and O surrounding the large bubble P appear to shrink in diameter as P appears to expand. It should be noted that several other bubbles very close to bubble P do not show a change in size. It is unclear why only bubble N and O decreased in size. Perhaps only the shells of these bubbles were damaged during the change in pressure or perhaps as Fagerlund (1990) suggested, bubbles of this intermediate size are not yet affected by the pressure differential. Furthermore, voids N and O decreased to a certain size and then stabilized. This is the same general behavior observed in the non air-entrained paste shown in setup #2 and had been observed by Mielenz et al. (1958A). While cracking of air-bubble shells was observed many times in this present experimental series, there were insufficient observations to conclude that a change in bubble diameter is typically associated with cracking of the shells.

As an interesting potential consequence of the observation of changes in bubble size, consider that the air bubbles observed here in water-suspension may be similar to those in cement paste that are surrounded in-place by a water filled "gap," as observed by others (Rashed and Williamson, 1991A, 1991B; Corr et al., 2002) . It would then seem plausible that gas permeability of the bubble shell would influence gas interchange

among bubbles of various sizes and internal pressures as also proposed by Mielenz (1958A) and Fagerlund (1990). This interchange could lead to a decrease in volume of the smaller bubbles and an increase in volume of the larger bubbles as observed in the experimental work in this paper. This change in void volume could ultimately lead to a higher overall air content in the mixture as first suggested by Mielenz et al. (1958A). This phenomenon could be an explanation for observations of increased air contents (i.e., higher air contents measured in hardened concrete as compared to air contents measured in fresh concrete using a pressure meter(ASTM C 231) as reported in field concrete (Hover, 1989) and in past research (Mielenz et al., 1958A; Gay, 1982).

6.4 SUMMARY OF KEY OBSERVATIONS

In this paper, some background is presented on the changes in a static air-void system in concrete and paste. Results from three different setups are presented that may provide insight into the fundamental behavior of air bubbles in water that have escaped from air-entrained and non air-entrained pastes. The degree to which these observations pertain to actual air bubbles fully surrounded by cement paste remains to be determined. It is pointed out, however, that the Air Void Analyzer (Jensen, 1990), the relatively new and interesting method for evaluating air bubbles in fresh concrete, liberates air bubbles into a water-glycerine solution in a far more energetic manner than was done in these experiments, and the bubbles thus liberated are considered by proponents of the method to be representative.

1. An opaque “shell” was observed on the exterior of air bubbles that had escaped from air entrained paste. The appearance of the shell changed as different AEA admixtures were used.

2. In these experiments with bubbles in bleed water, bubbles with an opaque shell appeared to resist coalescence, whereas translucent-to-transparent bubbles coalesced readily. Similarly, the shell appeared to take on structural properties such as stiffness, resistance to deformation, and eventual cracking. The role of these properties in stabilizing air bubbles within cement paste has not been identified.

3. When the shell appeared to be fully intact over observable portions of the bubble surface, the diameter of the bubbles did not change with time for the conditions of setup #2. When a readily discernable shell was not present as in the specimen of non air-entrained paste in setup #2, the diameter of the air bubbles was observed to change with time. Likewise, of those bubbles with a readily observed shell, only those that had cracked changed diameter with time.

4. In pressurized experiments shown in setup #3 it was observed that the air-bubble shell was damaged during depressurization from 0.7 bar to atmospheric pressure. This may be important in construction applications in which the concrete pressure is increased and decreased. It is not known, however, whether the experimental observations made here under a relatively mild and slow pressure change apply equally to the much higher pressure differences and rates of pressure change experienced in concrete pumping, for example.

5. A single shell-covered bubble that had escaped from air-entrained paste was observed to decrease in volume under pressure precisely as would be predicted by Boyle's Law, with no apparent influence of the shell.

The observations reported here have been of air bubbles suspended in a surrogate bleed water above paste. These observations may or may not be valid in concrete, and

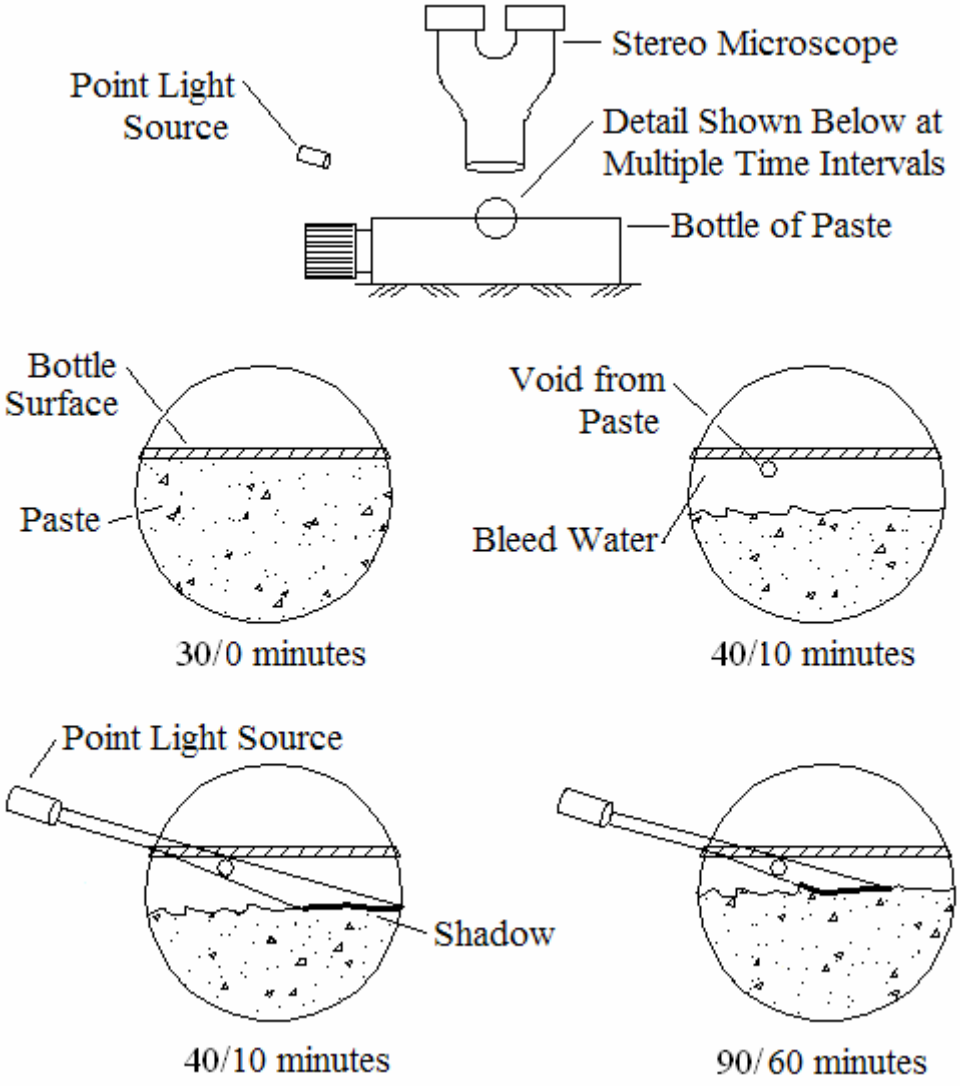
more research is clearly needed in this interesting and critical area of the stability of air bubbles in fresh concrete. Nevertheless the role played by what appears to be a shell of sorts at the periphery of air bubbles in air entrained concrete deserves attention.

Table 6.1 – Summary of previous research completed on air-void stability and the bubble shell.

reference and year	samples	method of observation	key observation	primary conclusion
Meilenz et al., 1958A	paste w/cm 30 AEA/lime/sand/cement combinations	stereoscope	bubbles change size with time and appear to have precipitates on the surface	pressure differential exists beween bubbles
	paste w/cm 0.3 - 0.6 prepared in drum mixer	ASTM C 457	hardened air volume was higher then fresh; descrepancy was larger with higher w/cm	gas interchange is occuring between bubbles
	concrete w/cm 0.45 prepared in drum mixer	ASTM C 231	hardened air volume lower then fresh	
Bruere, 1962	paste 0.45 w/cm prepared with 1000 RPM stirrer set of mixture modified to 5 min, 3, and 8 hours	ASTM C 457	no difference in air-void system between samples	no gas interchange between bubbles
Powers, 1968	---	---	how can bubbles increase in size if they are confined by paste?	doubtful if bubbles change size in paste
Rashed and Williamson, 1991A, 1991B	mortar w/cm 0.30 concrete 0.29-0.49 w/cm 3 hr-3 day w/ and w/o silica fume	frozen in liquid nitrogen and observed in LTSEM (mortar), SEM (concrete)	hydration products around air-void appear to be different mophology then bulk paste; shell observed at 5 min and 3 hour; shell made up of fine particles; gap between particles and shells vary in size and appear to contain water during hydration	shell likely made up of hydration products
Corr et al., 2002	bubbles isolated by AVA less than 30 min	frozen in liquid nitrogen and observed in LTSEM	"mineral" shell seen on individual bubbles and in the paste	shell observed in individual seperation technique similar to one found in paste
	paste w/cm 0.4 at 5 min		high porosity transition zone "often" observed around bubbles with a 10-15 μm thickness	transition zone may be increased by freezing

Table 6.2 – Mixtures investigated

mixture	admixture	dosage (ml/100 kg cm)	setup
1	none	---	1,2
2	synthetic	47	1,2
3	tall oil	143	1,2
4	wood rosin	48	1,2,3
5	Vinsol resin	18	1,2
6	Vinsol resin water reducer	26 81	3



The time is displayed in minutes after initial mixing and time after the bottle was placed on its side.

Fig. 6.1 –Setup #1 showing orientation of bottle, stereoscope, and point light source.

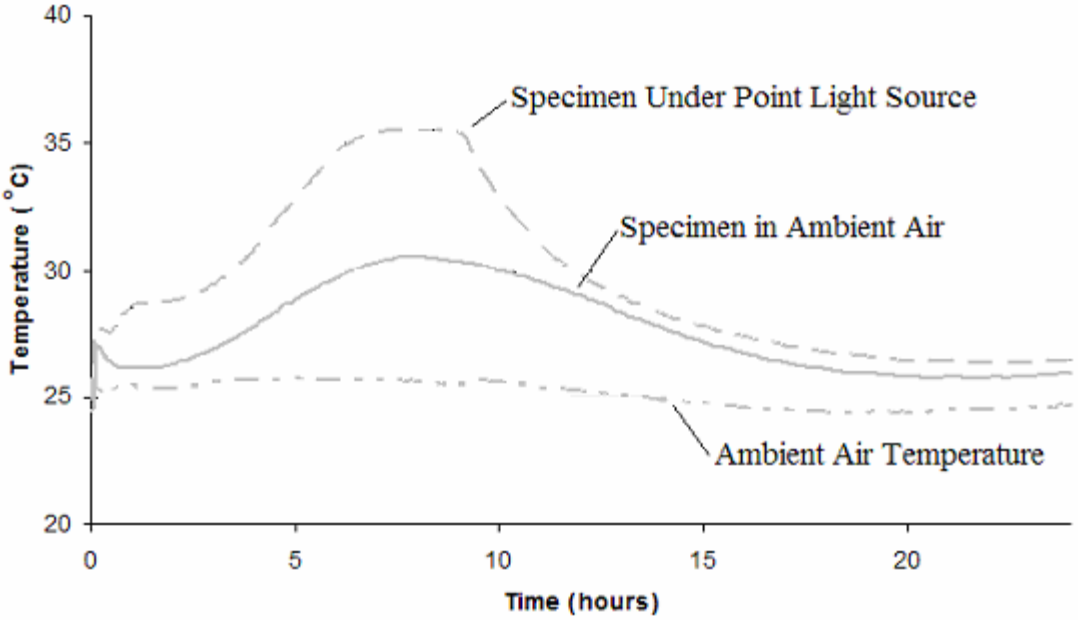


Fig. 6.2 –Time and temperature for the ambient temperature, a specimen under the point light source, and a specimen in the ambient temperature.

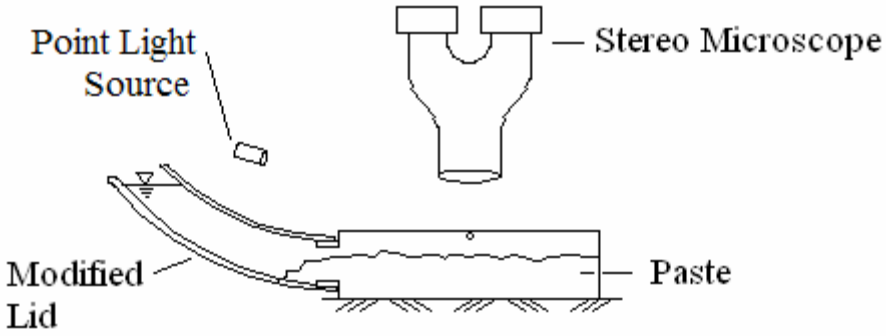
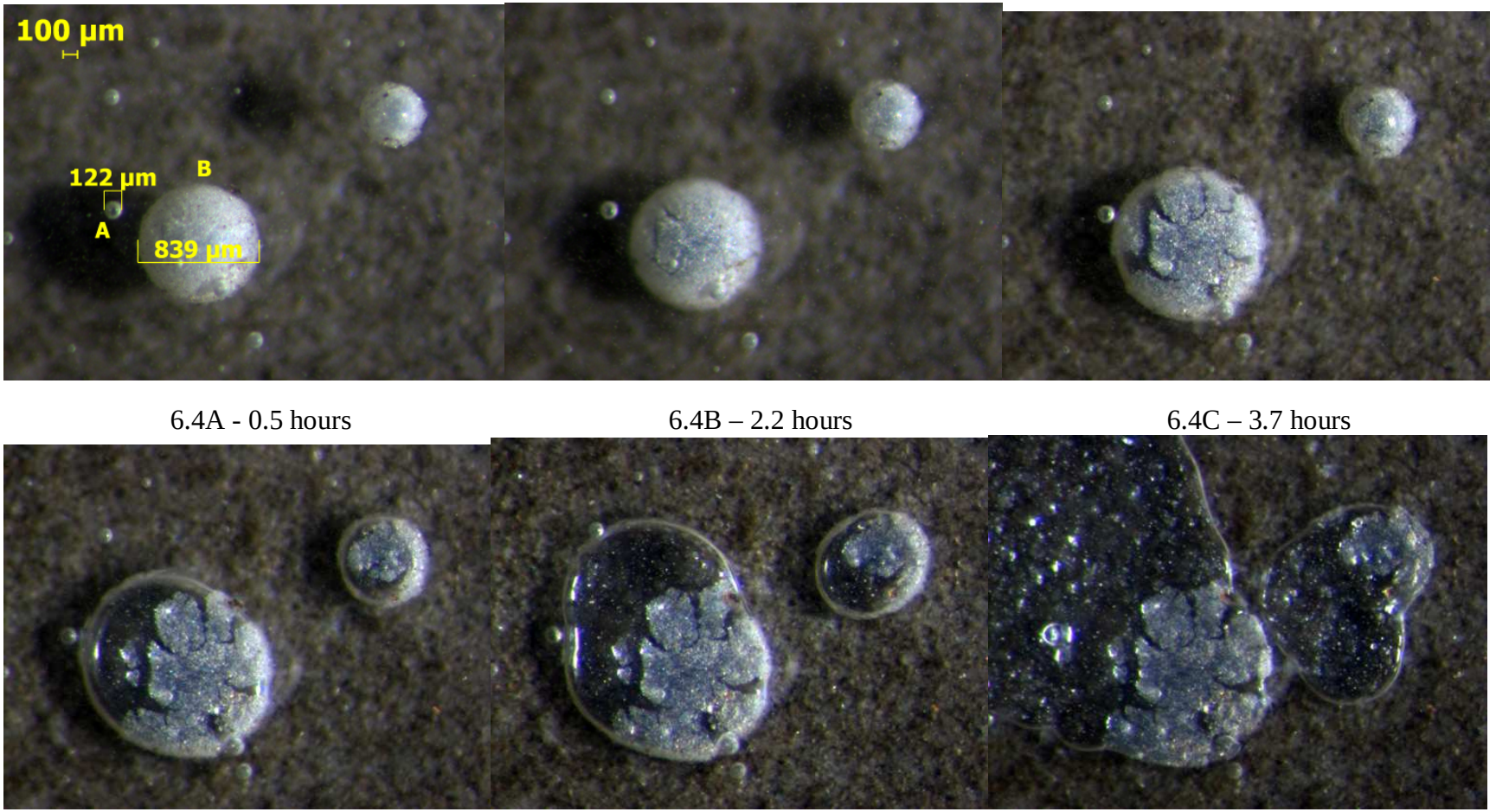


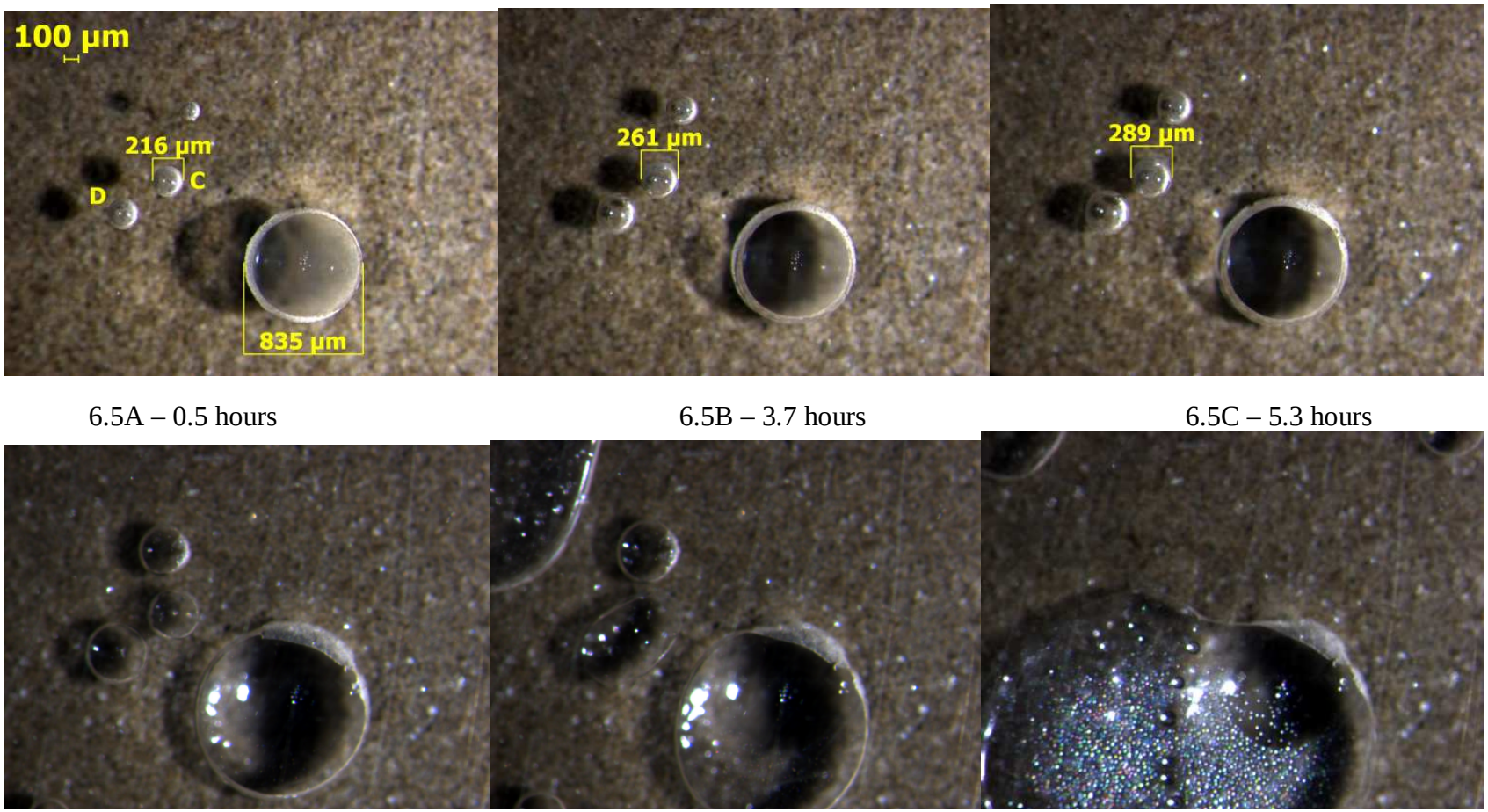
Fig. 6.3 – A cross section of setup #2 showing the reduced paste level and additional water provided by the tube with the modified lid.



6.4A - 0.5 hours | 6.4B – 2.2 hours | 6.4C – 3.7 hours

6.4D – 4.8 hours | 6.4E – 5.5 hours | 6.4F – 6.6 hours

Fig. 6.4 – An air-entrained paste containing a tall oil AEA at 143 mL/100 kg cm in setup #1 whose bubbles are pushed by the paste below.



6.5A – 0.5 hours

6.5B – 3.7 hours

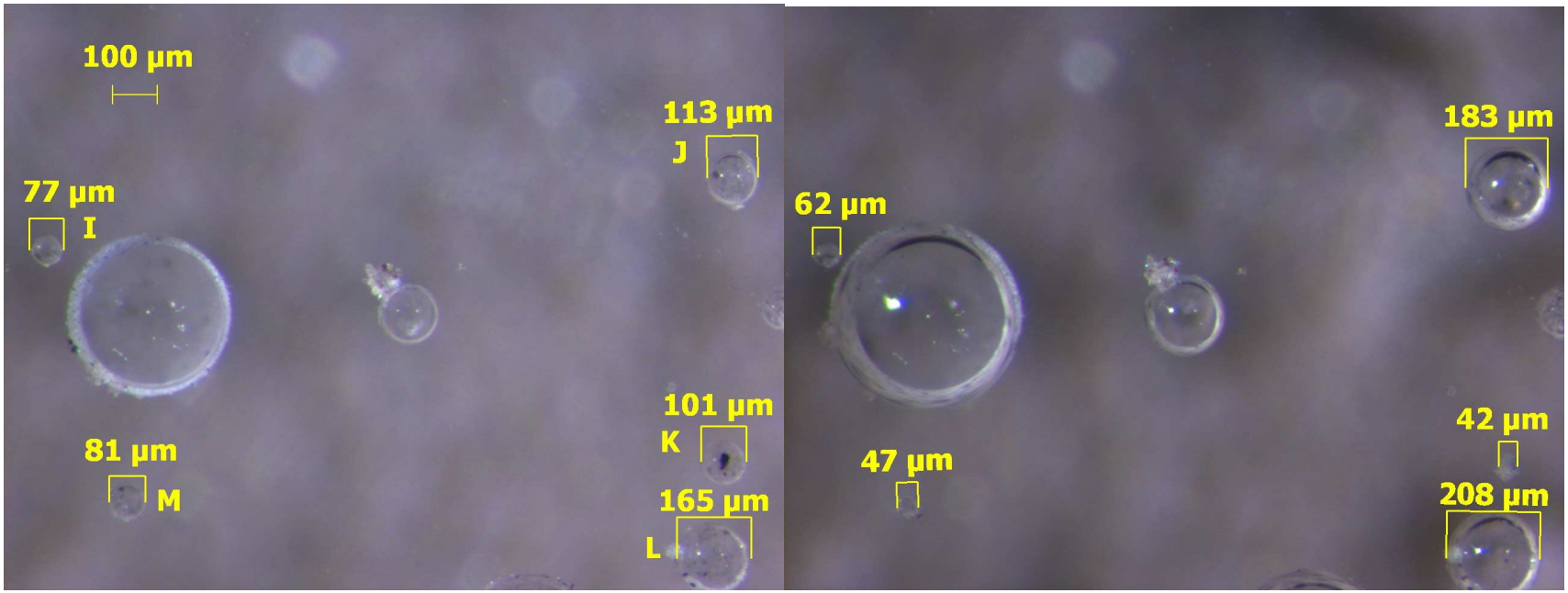
6.5C – 5.3 hours

6.5D – 6.8 hours

6.5E – 7.3 hours

6.5F – 7.8 hours

Fig. 6.5 – A non-air-entrained paste sample in setup #1 whose bubbles are pushed by the paste below.



6.6A – 0.5 hours 6.6B – 3.6 hours

Fig. 6.6 – A non-air-entrained paste sample in setup #2. 6.6A is taken 0.5 hours and 6.6B is taken 3.6 hours after hydration began.

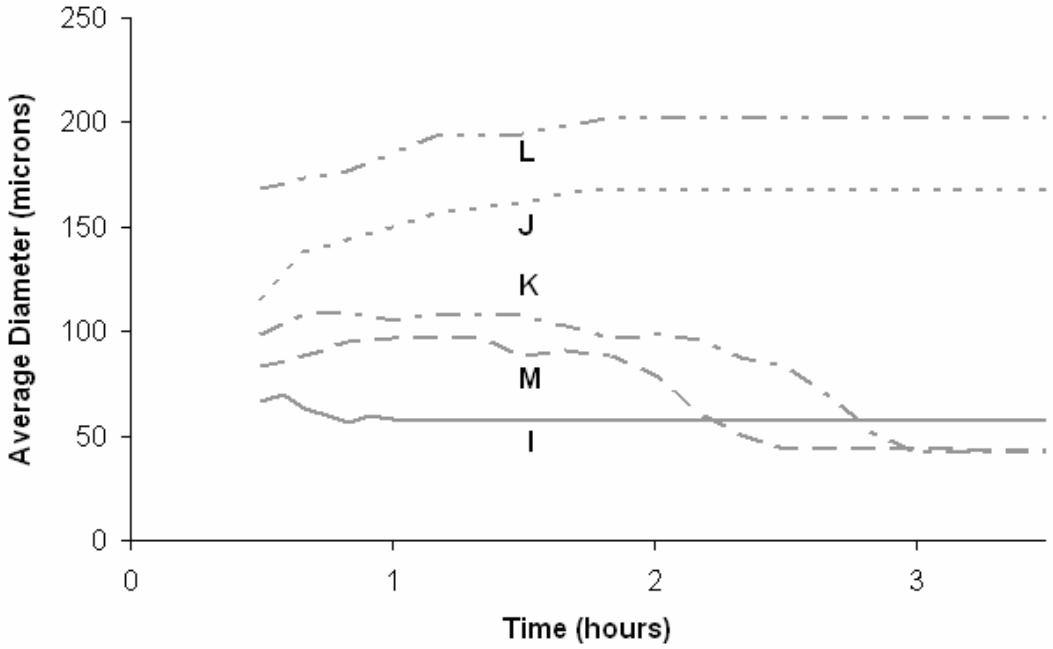
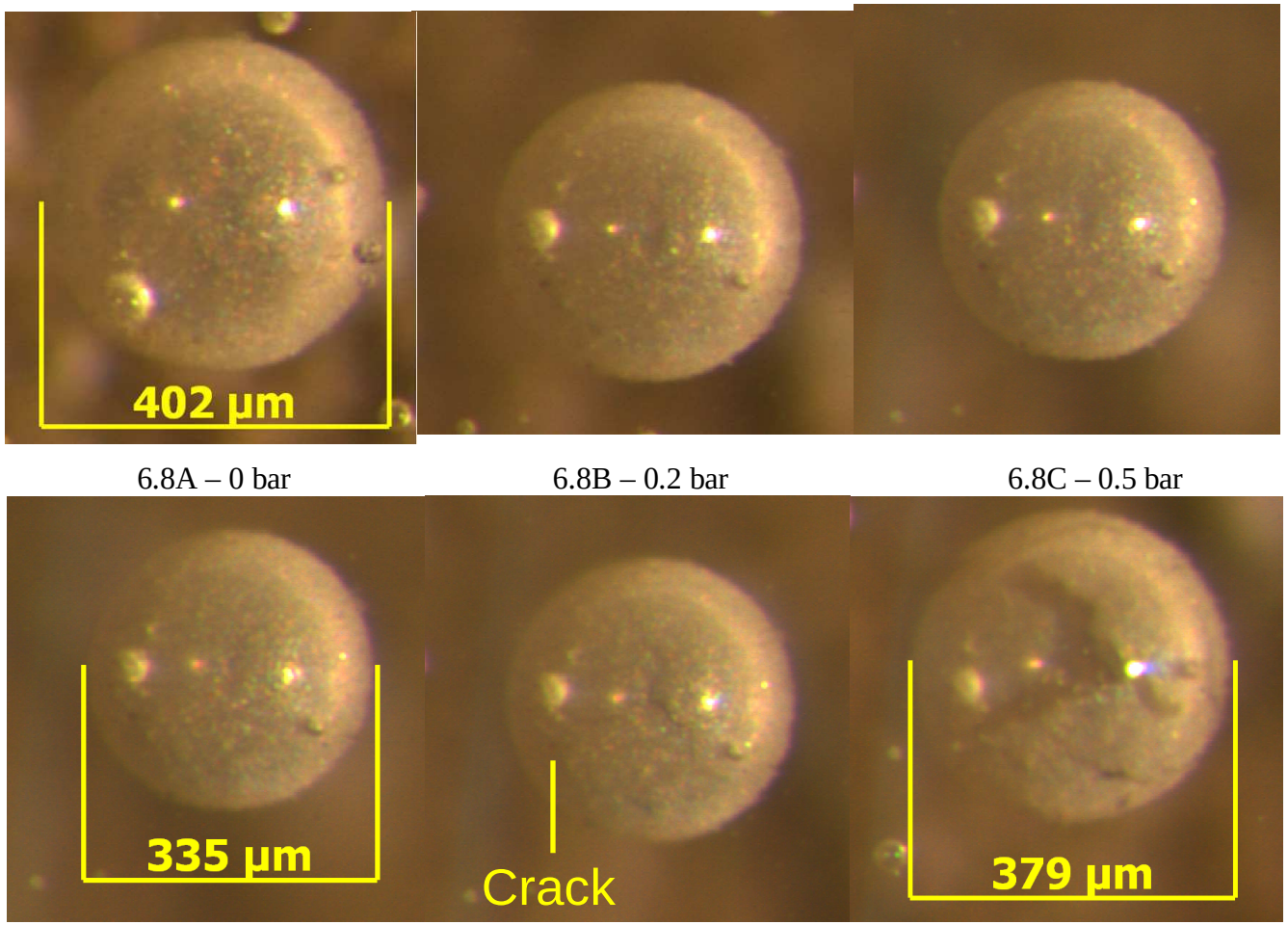


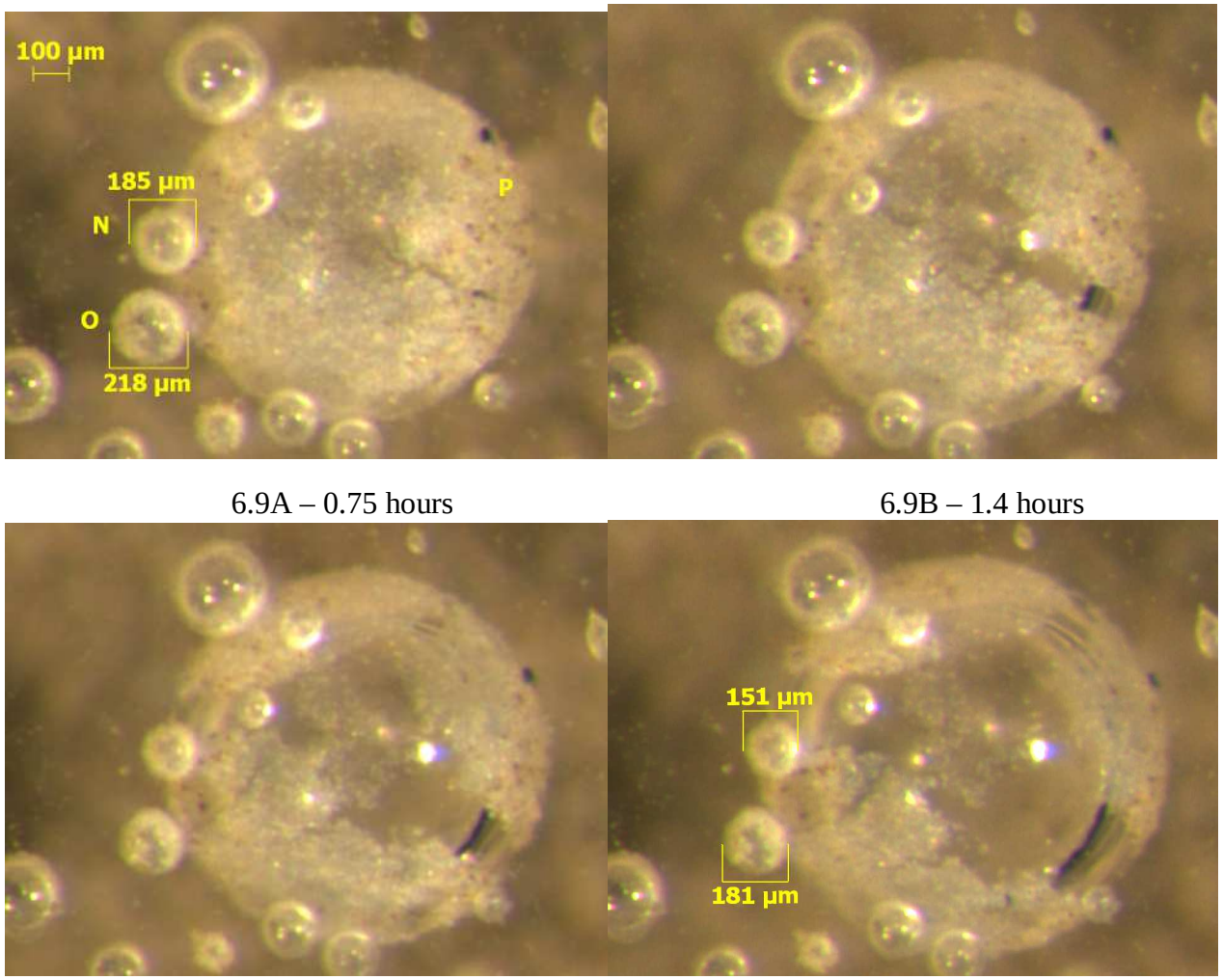
Fig. 6.7 – Average diameter of bubbles in a non-air-entrained paste specimen as shown in Fig. 6.6 in setup #2.



6.8A – 0 bar 6.8B – 0.2 bar 6.8C – 0.5 bar

6.8D – 0.7 bar 6.8E – 0.3 bar 6.8F – 0 bar

Fig. 6.8 – The response of bubbles escaped from a mixture containing 26 mL/100 kg cm of Vinsol resin and 81 mL/100 kg cm of normal WR subjected to a pressure 0.7 bar above atmospheric and then returned back to atmospheric pressure.



6.9A – 0.75 hours

6.9B – 1.4 hours

6.9C – 1.8 hours

6.9D – 3.4 hours

Fig. 6.9 – An air-entrained paste sample with wood rosin AEA at 48 mL/100 kg cm in setup #3.

Chapter 7: The Physical and Chemical Characteristics of the Shell of Air-Entrained Bubbles in Cement Paste

7.1 ABSTRACT

Recent research has suggested that the shell of an air-entrained void is important for resisting coalescence between air-voids and diffusion of gas from the surrounding fluid. The current paper describes the physical and chemical properties of an air-void shell during the first two hours of hydration and chemical characteristics at 60 days. Results from this research suggest that the air-void shells found in air-entrained paste have varied physical properties and the crystalline material of these shells is largely made up of fine cement particles and calcium carbonate ($CaCO_3$) during the first two hours of hydration. Observations of paste at 60 days of hydration suggest that the shell is made up of calcium silicate hydrate (C-S-H) with a morphology and stoichiometry different from that in the bulk paste.

7.2. INTRODUCTION

Air-entrainment is the primary method to provide resistance to damage from freezing and thawing and salt scaling in concrete in North America. Extensive research has been performed on the bulk properties of air-entrained concrete and the distribution and volume of air-entrained bubbles. However, very little work has been done to investigate the fundamental behavior and properties of an air-entrained void and its surrounding shell. These shells have been suggested in chapter 6 to be important in resisting the diffusion of gas into an air-entrained void from the surrounding fluid. This diffusion of gas is important as it suggests the small air-voids may diminish with time in fresh cement paste and lead to the increase in size of the more coarse air-voids and total volume of air (Mielenz, et al., 1958A). This phenomenon could explain the occasional

discrepancy between the measurements of the total volume of fresh and hardened air content as reported by several workers (Hover, 1989; Gay, 1982).

The goal of the present study was to investigate possible changes in air-void size and volume in fresh paste as suggested by Mielenz et al. (1958A). A further goal was to characterize the nature of the air-void shell that governs this behavior. This paper presents investigations of the relevant physical properties of air-entrained voids and their response to outside stress. Furthermore, x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive x-ray analysis (EDXA) are used to determine the chemical properties and morphology of the air-void shell at times of less than two hours and at 60 days.

7.2.1 Background

A review of the limited literature on the composition of air-void shells yields various hypotheses of their origin and makeup. Unfortunately very little supporting experimental work exists on this topic. In some of the earliest work done to investigate the fundamental characteristics of an air-void system in concrete, Mielenz et al. (1958A) photographed air-entrained voids in dilute pastes (i.e. high water-to-cementitious material ratio (w/cm)) with the aid of an optical microscope. These pictures showed that the perimeter of the air-entrained voids was covered by an early hydration shell. It was suggested that these shells could be made up of either a precipitated solid or gelatinous film from the calcium salts of the air-entraining agent (AEA) or metal ions contributed from the hydrating cement paste. The mechanism suggested by Mielenz et al. (1958A) to describe the shell formation is that the calcium salts of the AEA are soluble when the material is mixed in the bulk paste but could precipitate once concentrated around the air-water interface. To demonstrate this behavior, common AEAs were mixed with saturated lime-water and a white and brown insoluble precipitate formed. It was suggested that this insoluble material comprises the air-void shells. Mielenz et al. (1958A) also observed that cement particles were attracted to the surface of the air-entrained void.

Dodson (1990) pointed out that all commercially available AEAs are anionic in nature. This suggests that the hydrophilic portions of the surfactant molecules align themselves preferentially around the perimeter of an air-void and that these molecules are negatively charged. Dodson also suggested that the calcium ions, with their high charge density, are attracted to the negatively charged, hydrophobic ions stabilizing the bubble and these react to form an insoluble calcium salt, which was suggested to be a calcium rosinate. However, Dodson did not provide any experimental evidence to support this hypothesis. A study by Pigeon and Plante (1990) that utilized SEM with microprobe analysis on specimens prepared with high dosages of alkaline salts suggested that there were increased concentrations of sodium and potassium ions around air-entrained voids. The concentration was much larger than would be expected to be provided from the AEA and larger than that measured in the bulk cement paste. However, calcium ion concentration was not investigated in this study and the methods utilized did not allow observations of the bulk paste.

Several other studies investigated the mechanisms of freeze-thaw damage and the characteristics of air-void shells (Rashed and Williamson, 1991A, Rashed and Williamson 1991B; Corr et al., 2002). These studies featured samples whose hydration had been stopped by cryogenic freezing. The samples were then investigated in a low temperature scanning electron microscope (LTSEM). A technique was also developed that allowed the air-voids to be separated from the paste and then frozen and investigated with the LTSEM. Upon freezing, these air-voids were largely irregular in shape and seemed to be made up of heterogeneous fine particles that were between 1 and 5 μm. The researchers hypothesized that the particles surrounding the air-voids at least partially consist of unhydrated cement particles (Corr et al., 2002). Observations were also made of the morphology and interface between the air-void shells and the bulk paste (Rashed and Williamson, 1991B, Rashed and Williamson 1991B; Corr et al., 2002). The hydration products were suggested to be very dense over the 1-2 μm shell and a 10-15

μm water-filled space seemed to exist between the shell and the bulk paste. This gap was reported to increase in size as the w/cm of the mixtures increased and decreased in size with increased hydration.

7.3 EXPERIMENTAL METHODS

Due to the lack of available information regarding the basic physical and chemical properties of the air-void shells in concrete, an experimental program was developed to better characterize this material. In this study, several physical properties of the shells were investigated using a novel technique of isolating the bubbles in bleed water and then examining their response to stress. The behavior of the bubbles was captured with a digital camera fitted to a stereomicroscope at 50x magnification.

Chemical properties of the shell were also evaluated over the first 2 hours of hydration and at 60 days of hydration with the use of XRD and SEM with EDXA. The goal of this study was to investigate the microstructure and composition of the air-void shell and how they change with time with the hopes that this would lead to a better understanding of the behavior of the air-void shell and how it can ultimately be improved.

All of the specimens in this study were produced with a 0.42 w/cm paste using 1.37 kg of cement meeting the ASTM C 150 specifications for Type I and II with a 0.53 alkali content (Na_2Oeq). The phases of the cement were determined by Rietveld quantitative x-ray diffraction (RQXRD) (Rietveld, 1969; Stutzman, 1996) analysis and are reported in Table 7.1 as the specimens at zero minutes of hydration. The mixer and mixing procedure used in this study met requirements of ASTM C 305. All other details of the specimens are given in the respective sections.

7.3.1 Physical Properties

All of the observations of physical properties of the air-void shells were made by using a novel technique to investigate air-voids in the bleed water of cement paste

contained in a bottle as shown in Fig. 7.1. More details can be found in chapter 6. The following is a short summary of the experimental technique:

After the mixing of the paste was completed, a funnel was used to transfer the material into a transparent polystyrene bottle. The bottle was filled in three equal volumes and agitated after each addition of paste by tapping on a table top. Care was taken to ensure the bottle did not have any large air-voids, and was filled to capacity. At this point, the cap was tightened and the bottle was placed horizontally. After sitting for approximately 10 minutes it was possible to observe a layer of bleed water forming at the surface of the paste (Fig. 7.1). In this bleed water, air-voids could be found that had worked their way to the surface of the paste due to their buoyancy. These voids were then observed and documented using a stereomicroscope fitted with a digital camera. A computer program was written to automatically capture images of the changes in these voids at specified intervals of time.

For some of the specimens, the same preparation technique was used; but an air pump was attached to the bottle of paste with a pressure regulator and gage. This allowed the fluid pressure inside of the bottle to be increased or decreased in any manner while the bubbles were investigated with the stereomicroscope and digital camera. The air-voids were investigated while they were subjected to an increase and then sudden decrease in fluid pressure similar to what might be imposed by a concrete pump.

With these experimental setups, the following physical properties of air-entrained bubbles were investigated: adhesion of cement particles, transparency, the response of bubbles to fluid pressure, and the ability of the air-void shell to repair after being damaged.

7.3.2 Chemical Properties during the First Two Hours of Hydration

In order to determine the chemical consistency of the air-void shell, the air-voids were separated from the paste at different time periods, in this case from eight minutes to two hours of hydration by injecting a 20 cm^3 sample of air-entrained paste into the

bottom of a tall column of water utilized by the Air-Void Analyzer as this provided an useful method to liberate the bubbles from the paste. A stirring rod at the bottom agitated the paste and the bubbles rose up the column. The bubbles were caught at the top of the column with an inverted watch glass. After collecting bubbles for three minutes, the watch glass was removed. The majority of the bubbles collected adhered to the watch glass surface. The excess water was removed from the watch glass with a syringe and the specimen was placed in a vacuum desiccator overnight. The dried material was scraped from the watch glass and stored under vacuum until the crystalline material could be analyzed by RQXRD. Because so little material was collected during the bubble separation (approximately 5 mg) it was necessary to use a standard height low-background quartz-disk specimen holder. The specimen holder was covered with a thin layer of petroleum jelly to insure the material would adhere to the holder. The sample was sprinkled onto the jelly and then spread out so a thin layer of material covered the surface. Care was taken to ensure that a low profile of powder was used for the sample, such that proper specimen height was maintained, thus minimizing sample-displacement error. A sample holder was also analyzed that was only covered in petroleum jelly and was found to give only slight background noise at low angles of investigation. This was determined to not impact the accuracy of the quantitative analysis.

This technique was utilized to analyze air-voids from pastes containing wood rosin and synthetic AEA dosed at 48 mL/100 kg of cement at various time intervals, up to two hours of hydration. A non air-entrained paste was also investigated after 30 minutes of hydration. The same cement was used for this testing as was used for examination of the physical properties of the air-voids.

Another set of tests was conducted on samples of hydrated cement paste obtained from a bulk cement paste containing 48 mL/100 kg of cement of a wood rosin AEA which was allowed to hydrate in the mixing bowl and was stirred by hand prior to a sample being extracted at time intervals of hydration from 8 minutes to 2 hours. No

petroleum jelly was used for this analysis as the paste was placed directly on the low-background sample holder at the reported time of hydration and then placed in a drying vacuum. It is unclear how long it took the water to be removed from the sample. While visual observations of the color change of the sample indicate that drying was complete within 5 minutes under vacuum, drying was allowed to continue overnight. A low-background sample holder was used so that the sample preparation between the two methods was kept as similar as possible. After the specimens were dried, the height of the sample was reduced to the clearance of the zero background sample holder in order to minimize the sample displacement.

Cement samples were also analyzed by preparing approximately 2 g of cement in a standard powder-mount sample holder. The RQXRD analysis was performed with a Siemens D500 x-ray diffractometer equipped with a DACO_MP digital controller and analog-to-digital signal converter. All samples were analyzed from 20° to 80° 2θ, with a step size of 0.02° and dwell time of 4 seconds/step. The atypically lengthy step provided a sufficient x-ray signal-to-noise ratio for rigorous quantitative analysis. A traditional 2200 watt copper (Cu) x-ray tube was used. The diffractometer was configured with a 1° divergent slit, a 4° soller slit, and a 1° antiscatter slit on the incident-beam side. A 1° antiscatter slit, a 4° soller slit, a single-crystal monochromator, a 0.15mm receiving slit, and a 0.6 mm detector slit were used on the divergent-beam side. Each pattern was analyzed using the whole-pattern fitting method developed by Rietveld (1969) and demonstrated for use in cementitious materials by Stutzman (1996) using the TOPAS-Academic software package.

7.3.3 Chemical Properties after 60 Days of Hydration

Air-entrained paste made with wood rosin AEA at 48 mL/100 kg of cement was allowed to hydrate inside of a bottle shown in Fig. 7.1 in a 100% RH environment for 60 days. The sample was fractured and a small flake about 2 mm thick of the now exposed, interior surface was examined for air-entrained voids using a SEM with EDXA. The

SEM used was a LEO 1530 Field Emission SEM equipped with an IXRF solid-state energy dispersive spectrometer. The operating voltage was 15kV, working distance = 11 mm, X-ray count rate = 400 cps, and EDXA dwell time = 60 seconds. The sample was sputter-coated with a 20 nm thick layer of silver to provide conductive continuity.

7.4 RESULTS AND DISCUSSION

7.4.1 Physical Properties

7.4.1.1 Adhesion of Cement Particles

In Fig. 7.2, a paste made with wood rosin AEA at a dosage of 48 mL/100 kg of cement is shown after 10 minutes of hydration. When the void leaves the cement paste and rises to the surface, one can clearly see a significant portion of cement paste is adhering to the air-entrained void and is also carried up to the surface of the bottle. While it is difficult to determine the volume of the paste that is attached to the void, it is obvious that the quantity is significant. This implies that the attraction between the cement particles and the air-entrained bubble is significant and may be measurable. This observation is not an anomaly and the adhesion of cement to air-entrained bubbles is regularly observable in the specimens investigated for this study. This observation confirms previous work by Mielenz et al. (1958A) and hypothesized by Corr et al. (2002).

7.4.1.2 Transparency

Air-voids from a paste with wood rosin AEA used at a dosage of 48 mL/100 kg of cement are shown in Fig. 7.3A. The air-voids shown in Fig. 7.3B are from a paste with no AEA. Both pictures were taken approximately 45 minutes after mixing. There is a significant difference in the transparency of voids in air-entrained and non air-entrained pastes, the former are translucent while the latter are transparent. This difference in transparency is likely attributable to the shell material that has been shown to exist around voids in air-entrained paste and is missing from voids in a non air-entrained paste.

These shells seem to be present at AEA dosages typically used in concrete. The translucent air-void shells were regularly observed for the following AEAs: wood rosin, Vinsol resin, tall oil, and synthetics. The appearance of the shells is different for each of the AEAs. Very little difference was observed for different dosages of AEA, but more work is needed in this area.

7.4.1.3 Bubble Response to Fluid Pressure

7.4.1.3.1 Vinsol Resin AEA

An air-void in the bleed water of an air-entrained paste with 26 mL/100 kg of Vinsol resin AEA and 81 mL/100 kg of a polymer-based normal range water reducer is shown at atmospheric pressure in Fig. 7.4A after 45 minutes of hydration. For this test, the fluid surrounding the air-void system was increased to 0.7 bar above atmospheric pressure in 10 equally spaced steps and then decreased back to atmospheric pressure in three equal steps. A selected number of images are shown in Fig. 7.4 with Figs. 7.4A-D showing the results of increasing pressure and Figs. 7.4E and F showing voids while the pressure is decreasing.

In Fig. 7.4D, one can see that the air-void has decreased in diameter by almost 20% at a pressure of 0.7 bar and yet the bubble does not appear to be distressed. As the pressure began to be released, it can be seen in Fig. 7.4E that the shell of the large air-void cracked as the volume of air increased inside the void. These cracks widen in Fig. 7.3F as the fluid was brought back to atmospheric pressure. This is significant as it has been previously proposed that after the air-void shell has been damaged, it is possible for an interchange of air to occur from the surrounding fluid, then a change in the air-void distribution and volume can occur (Mielenz et al., 1958A). It appears that some amount of air was lost to the surrounding fluid during the increase in fluid pressure as the final diameter is 6% lower than the initial diameter. Similar behavior was found for voids of a similar size stabilized by wood rosin AEAs. This behavior has been witnessed regularly

for voids that are larger than 200 μm. However, it is difficult to say whether the behavior occurs in voids that are smaller as they are difficult to observe at the magnification used.

7.4.1.3.2 Synthetic AEA

A void in the bleed water of air-entrained paste with 47 mL/100 kg dosage of a synthetic AEA and 85 mL/100 kg of normal range water reducer is shown in Fig. 7.5A after 45 minutes of hydration. The surrounding fluid pressure was increased to 0.7 bar in 5 equal pressure steps and then decreased back to atmospheric pressure in three equal pressure steps. Selected images are shown in Fig. 7.5.

At a pressure of 0.3 bar, the shell of the air-entrained void began to distort as shown in Fig. 7.5B. As the fluid pressure increased, so did the distortion of the void. It can be seen in Fig. 7.5C that the bubble was no longer spherical and had a significant crease at the center. Whenever the air pressure was reduced back to atmospheric the shell returned to a size within 5% of the original diameter. Also, during this increase and decrease in pressure, the shell of the void was never permanently damaged. This test was performed five times and the behavior was similar for voids larger than 40 μm. Voids smaller than this did not appear to show the same buckling of the shell; but it is very difficult to observe small voids at this magnification.

7.4.1.3.3 Differences in AEAs

It is clear that there is a significant difference in behavior between the synthetic and the Vinsol resin and wood rosin AEAs. The air-void stabilized with the synthetic AEA seemed to buckle as the surrounding fluid pressure was increased. This seems to imply that the air-void shell has some stiffness in compression and a substantial amount of elasticity in tension as the void did not crack when the fluid returned to atmospheric pressure. On the other hand, the air-void stabilized with the Vinsol resin was very elastic when the fluid pressure was increased and seemed to be very weak in tension. It is unclear why there is such a large difference in behavior between the two products.

However, this difference in behavior is possibly attributable to the difference in the molecular structure of the AEA or the resulting air-void shell, and thus the surrounding hydration products.

7.4.1.4 Self Repairing

In Fig. 7.6 an air-void above a paste containing 48 mL/100 kg of wood rosin AEA that has been pressurized to 0.7 bar and then depressurized to atmospheric pressure is shown over a 5.7 hour time period. As stated previously, the shell of air-voids in wood rosin systems crack while being depressurized. Fig. 7.6A shows a void with a cracked shell immediately after the return to atmospheric pressure. Over the next 0.4 hours the shell continues to crack and expose more of the underlying bubble, Fig 7.6B. This occurred while the bottle sat undisturbed. At 3.6 hours after hydration began, the shell around the air-void begins to reform, Fig. 7.6C. Pictures are shown of the shell reforming over the next 2.8 hours. In Fig. 7.6F an image is shown after 6.4 hours of hydration and it appears that the shell has repaired itself completely and no cracks are present.

If an air-void shell were able to self heal itself, then this behavior could provide a method for the air-void to recover from damage to the surrounding shell as previously shown with changes in pressure. One reason why the shell in Fig. 7.6 may have taken such a long period of time to repair itself was the large amount of damage that was done to it. If this damage had been less severe, then the repair might have taken less time. These observations may also help provide insight into the mechanisms of the initial air-void shell formation. Three other observations of self healing have been observed but none as dramatic as the one shown in Fig. 7.6. On the majority of the tests completed it was very difficult to see the shells being repaired as the cracks in the bubbles are small and the repairs seem to take less time.

7.4.2 Chemical Properties

7.4.2.1 Chemical Properties During the First Two Hours of Hydration

Table 7.1 contains a summary of the crystalline material analyzed in the air-void shells in pastes containing wood rosin and synthetic AEAs over time. Table 7.1 also contains results from analysis of the crystalline materials in the bulk paste. These data were obtained through RQXRD analysis. The data for the unhydrated cement indicate the composition of the starting material. Repeat specimens were run for the majority of the data points and the values presented in Table 7.1 are averages with standard deviations in parenthesis. While some variability was found, it was determined to not be significant for phases that were present in quantity greater than 10% of the overall crystalline material of the sample. Variability in RQXRD is generally on the order of at least 3% (Chancey, 2007).

All of the specimens analyzed contained the same crystalline phases; however, the amount of each phase present in the sample varied with sample type and time. The results indicate that there is very little change in the crystalline phases present in the bulk cement paste over the first two hours of hydration. This is not surprising since the onset of significant C_3S hydration is not expected in this time period at room temperature in the absence of accelerators. The increase in gypsum content may be a reflection of the hydration of hemihydrate and anhydrite. The changes in quantities of the other phases are within error and can be considered negligible.

For the specimens taken from the air-void shell material it was found that there was a significant change in the amounts of anhydrous material and $CaCO_3$ with time in the samples. The C_3S and $CaCO_3$ contents are shown graphically in Fig. 7.7. In each of the types of air-void shells it appears that there is less C_3S than in the original cement. In the wood rosin AEA shells, the C_3S content appears to decrease between 8 and 30 minutes, then remains constant. In the synthetic AEA shell, the amount of C_3S decreases from the initial amount found in the cement and then is constant with time.

Correspondingly, the percentage of other phases crystalline phases present are observed to increase with time. This is expected if a dissolution of C_3S is occurring. Another interesting observation is that the amount of $CaCO_3$ is higher in the air-void shells than in the original cement and increases with time up to 30 minutes. After 30 minutes the amounts of $CaCO_3$ remain constant. The increase in $CaCO_3$ seems to occur at an increased rate when the specimen is made with the synthetic AEA compared to wood rosin AEA, but they reach the same constant level with time.

The changes in anhydrous phases and the presence of so much $CaCO_3$ in the air-void shell material are unexpected. More discussion on these observations appears later in the paper. However, whatever the mechanism for the increase in $CaCO_3$ is it is likely tied to the reduction in the C_3S as they are occur simultaneously and proportionately.

7.4.2.2 Chemical Properties at 60 days of Hydration

An air-entrained void approximately 550 μm in diameter was found on a fractured hardened cement paste surface and investigated with a SEM with EDXA. A top view of the air-void is shown in Fig. 7.8A and magnified pictures of the air-void wall are shown in Figs. 7.8B-D. The interface between the air-void shell and the bulk paste is shown in Fig. 7.9A and at increased magnification in Fig. 7.9B. From Fig. 7.9 it appears there is a 1μm thick shell of hydration product is surrounding the air-void. Just adjacent to the shell there appears to be a discontinuity between the phases in the shell and the bulk paste of the sample, similar to the observations mentioned previously (Rashed and Williamson, 1991A, Rashed and Williamson 1991B; Corr et al., 2002),. The shell seems to be made of a very dense hydration product. Furthermore, it seems small crystals are growing on the surface of the void. Visual and EDXA analysis suggest that these crystals are ettringite.

The air-void surface in Fig. 7.8B is shown in Fig. 7.8C and 7.8D under increasing magnification. At this high magnification one is able to closely examine the very dense microstructure of the air-void shell. To investigate the chemical composition of the

shell, the area shown in Fig. 7.8B was investigated with EDXA. The surface analyzed was approximately 185 μm x 135 μm. Since this analysis is taken over a large area it should be representative of the chemical makeup of the void surface. EDXA gives information on the relative amounts of the elements present. The ratios of the peak heights can be compared to find the relative quantity of each element. It was determined that the majority of the sample was made primarily of calcium and silicon. Trace amounts of aluminum and sulfur were also found. The ratio of calcium-to-silicon of the air-void shell was equal to 1.1. This is lower than what is expected for a typical C-S-H found in bulk cement paste. When the EDXA was used to investigate C-S-H found in the bulk paste of this sample, the calcium-to-silicon ratio was found to be 1.5. The ratio for the C-S-H of the bulk paste agrees with numbers given by Pigeon and Plante (1982) and Diamond (1976) for the method used.

EDXA seems to indicate that the air-void shells consist of C-S-H with small amounts of ettringite needles on the surface of the void. The air-void hydration shell shown in Fig. 7.9 seems to be denser than the C-S-H found in the bulk paste. This can be seen in Fig. 7.9 if one looks at the large number of voids in the hydration product formed adjacent to the shell in comparison to the shell itself. The shell thickness and presence of a "transition zone" confirms results from Corr et al. (2002).

7.5 DISCUSSION OF MECHANISMS

RQXRD showed that the early composition of the air void shell is very similar to the bulk cement paste but with a lower C_3S content, higher amounts of other anhydrous phases, and higher $CaCO_3$ content. These differences are unexpected and merit further discussion. The ability to understand the chemistry of these air void shells is critical in order to improve the performance of air entraining agents and understand the observed behavior.

The charge imparted by the anionic AEA on the outside of the air-entrained void may be significant in explaining the composition of the air void shell. This anionic

charge likely contributes to the adhesion of cement particles to the air void. The surfaces of cement particles are charged, causing an attraction between the particles and the outside of the bubble. This attraction results in cement particles adhering to the bubble as shown in Fig. 1 and as suggested by others (Mielenz, 1958A; Corr et al., 2002). This also results in the high quantities of anyhydrous cement phases measured in the bubble shell at early ages through RQXRD. The only way that anhydrous phases would be present in the shell is through adhesion of the particles to the bubble.

If the early hydration shell were made up completely of adhered cement particles, then the shell composition would be identical to the unhydrated cement and, correspondingly, the bulk paste since it does not differ significantly from the unhydrated cement at the times examined. However, the amount of C_3S in the shells is much lower than the amount of C_3S in the anhydrous cement and bulk paste. If all anhydrous phases were present in lower amounts in the shell, then one could assume that the ratio of cement-to-reaction products in the shell is lower than in the paste. However, the relative proportions of the other anhydrous phases are higher in the shell than in the original cement. One possible explanation for this difference is that the C_3S dissolves more rapidly in the cement particles attached to the air void. This explanation is consistent with the decrease in C_3S and increase in all other analyzed phases. Since all analyzed phases must add up to 100%, a decrease in one phase must be matched by increases in all of the others.

The anionic surface charge may also play a significant role in the mechanism of this rapid decrease in C_3S. The dissolution of C_3S into solution initially occurs rapidly in water. This dissolution has been suggested to subside when the surface of the C_3S changes, beginning the induction period (Gartner et al., 2002). While different theories exist about the mechanism of the reduction in the rate of early C_3S dissolution, one by Barret and Menetrier (1980) suggests that the dissolution of the C_3S surface results in a net positive charge on the particle. In the bulk cement paste this surface charge is

thought to be balanced by hydroxyl ions which block further dissolution until a critical concentration of calcium and silicon is reached. If this were the case, then the negative charge of the air-void surface may neutralize this surface charge and allow C_3S dissolution to continue in this region without an induction period. This would explain the observed rapid decrease in C_3S content in the air void shell. As the C_3S dissolves, an early C-S-H may be nucleating on the air void, giving the shell the physical characteristics observed. With time, the surface charge on the air-void shell is likely reduced from this C-S-H formation, decreasing the ability to control the surface charge of the C_3S and the induction period begins. This would explain the reduced rate of dissolution and the beginning of the induction period for the C_3S.

As explained previously it appears the C_3S is dissolving or leaving the surface of the air-void as all other phases in the analysis are shown to increase. However, the $CaCO_3$ in the analysis showed a much more significant increase compared to the other phases and this increase appears to be proportional to the decrease in C_3S. It is unclear the source of this increase but they appear related. One possibility is that calcium ions released from the dissolving cement may concentrate at the charged air-void shell surface, since it is negatively charged, as discussed earlier. These free calcium ions may react with carbon dioxide that is dissolved in the mixing water, water column used to separate the air-voids from the paste, or from the air contained in the air-void to form the $CaCO_3$. For this mechanism to be satisfactory then the C_3S in cement would need to contribute calcium ions to the formation of $CaCO_3$ and to the formation of other hydration products. This may be possible as the EDXA on the 60 day old air-void shell suggests that the C-S-H formed on the air-void shell has a low calcium content which could allow the remaining calcium ions to contribute to the formation of the $CaCO_3$. It should also be noted that there was no portlandite (CH) in the air-void shell or in the paste during the two hour fresh testing period. This is not surprising, since the induction period had not ended and CH generally does not precipitate during this period.

Therefore, CH formation is not competing with $CaCO_3$ for calcium ions which would permit it to form.

It was also observed in this study that the use of a synthetic AEA resulted in a much more rapid decrease in C_3S content than with the wood rosin AEA and displayed different physical properties. This difference in performance is likely attributable to differences in the chemical nature of the surfactants used in the different AEA products. This could be from differences in surface chemistries that promote the hydration or dissolution of C_3S. However, without detailed knowledge of the nature and concentration of the compounds utilized in these products it is difficult to make comments on their difference in performance. The ability to understand how differences in these surfactants change the performance of the air-void shell is crucial to improving the performance of existing products.

It should be noted that the explanations offered for the changing composition of the air void shells are speculative and it is possible that the chemistry of the shells is controlled by mechanisms other than those suggested here. This is an area that certainly merits further research.

7.6 CONCLUSIONS

This paper presents the results of an investigation into the physical and chemical properties of air-void shells. The results are not meant to be conclusive; a large amount of information remains unknown. However, several new insights have resulted from this work.

- It has been shown that there is a strong adhesion between cement particles and air-voids beginning at the first minutes of hydration.
- It appears that there is a large difference in transparency between the air-entrained and non air-entrained voids as well as a difference in the ability of the voids to resist size changes with time.

- There is a significant difference in performance between the resulting shells with different AEA admixtures when the fluid pressure surrounding voids is increased and then decreased again to atmospheric pressure. Voids made with synthetic AEA sustain no permanent damage, while voids made with Vinsol resin and wood rosin crack on depressurization.
- The cracks in a wood rosin void shell were observed to self-heal.
- The amount of C_3S present in the air-void shell is lower than in the original unhydrated cement and the bulk paste This effect may be due to delays in the induction period for the C_3S particles at the air-void surface.
- The increase in $CaCO_3$ in the air-void shell in the first two hours of testing may be an artifact of the sample preparation technique as it was not observed in the SEM analysis of the 60 day old air-void shell.
- The rate of C_3S decrease and $CaCO_3$ increase is faster for synthetic AEA than for wood rosin AEA. It is likely that this difference in hydration rate is related to the difference in behavior of the air-void shells of the different AEAs.
- SEM observations and EDXA of the air-voids in the 60-day-old cement paste showed that the surface of the air-void seems to be predominately made up of a C-S-H phase that is of a different stoichiometry than that found in the C-S-H of the bulk paste as the ratio of the calcium-to-silicon of the air-void shell is around 1.1 compared to 1.5 as found in the bulk paste.

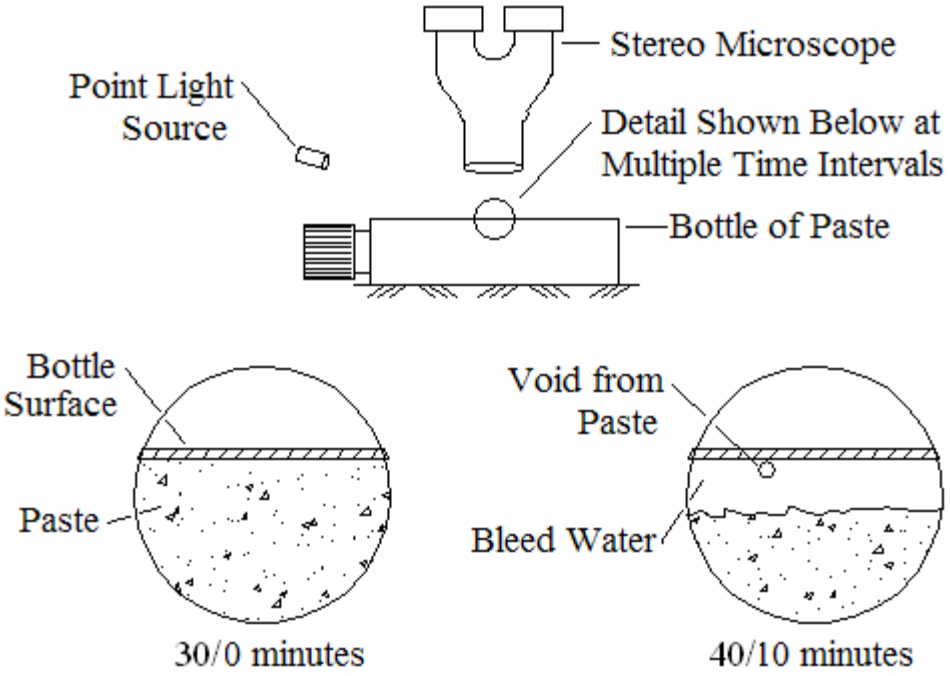
While this paper showed several unique physical characteristics of air-entrained void shells, more work is needed to better characterize the chemical makeup of this material. The majority of the work done in this paper to chemically characterize the air-void shells focused on the crystalline material found in the shell. While the findings are helpful, no data are presented regarding the amorphous materials involved as no analytical techniques are currently readily available to the authors to analyze early

amorphous hydration products in these shells. Characterization of the amorphous material is needed before any final conclusions can be drawn. If one were able to fully and accurately characterize the shell material then it may be possible to explain why the AEA voids have their respective physical properties that change with time, pressure, and AEA composition. It may also be possible to engineer new surfactants that could improve the performance of air-entrained concrete.

Table 7.1- Summary of the RQXRD analysis for the air-void shells and bulk paste.

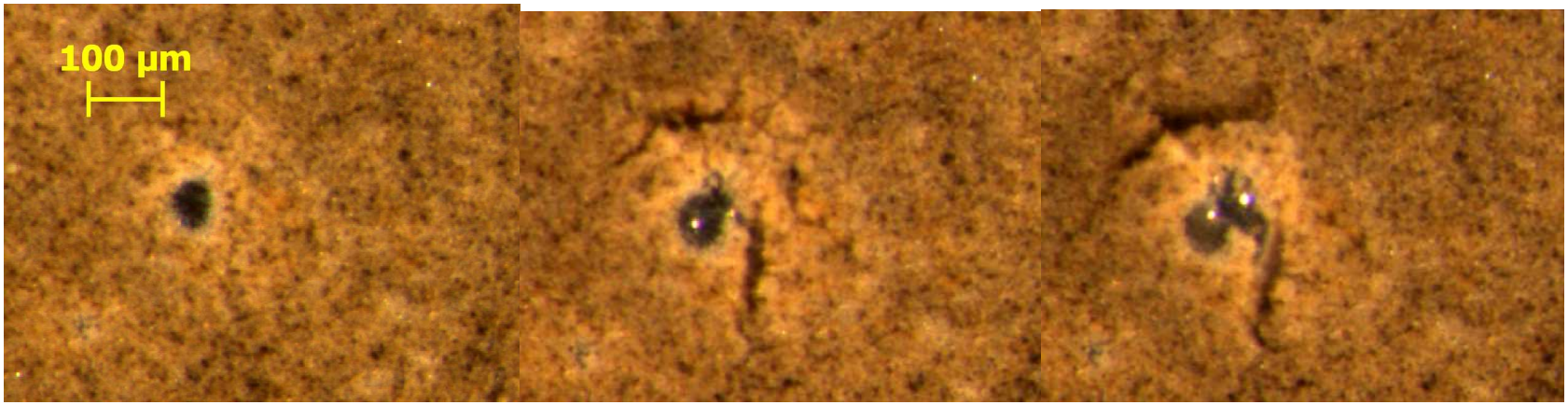
	Time	C_2S %		C_4AF %		C_3A %		$CaCO_3$ %		C_3S %		Ettringite %		Gypsum %	
wood rosin	0	15.7		8.7		2.7		2.6		68.0		0.8		1.3	
	8	17.6	(0.8)	13.6	(1.2)	5.6	(0.9)	8.0	(0.8)	50.5	(2.4)	2.6	(2.1)	2.0	(1.4)
	30	20.9		16.4		4.3		12.7		38.2		5.3		2.2	
	45	18.9	(4.0)	14.7	(0.6)	5.8	(1.6)	14.7	(3.0)	41.6	(0.4)	1.3	(0.3)	3.2	(0.1)
	90	20.7	(1.5)	16.5	(0.5)	5.5	(1.2)	14.1	(0.9)	38.3	(0.5)	2.2	(2.5)	2.8	(0.4)
	120	22.5	(3.9)	16.5	(1.6)	5.2	(1.2)	14.6	(2.7)	35.5	(6.5)	4.1	(3.3)	1.6	(0.8)
synthetic	0	15.7		8.7		2.7		2.6		68.0		0.8		1.3	
	8	18.2	(0.2)	18.8	(2.7)	4.7	(0.4)	21.9	(5.7)	33.1	(9.5)	0.9	(0.4)	2.4	(1.0)
	30	16.0	(0.7)	14.6	(1.4)	6.6	(0.4)	20.8	(3.9)	36.1	(5.5)	3.8	(0.1)	2.1	(1.2)
	45	15.4	(0.4)	18.0	(5.8)	5.0	(1.3)	18.6	(6.2)	38.7	(12.8)	1.7	(1.1)	2.7	(2.8)
	60	18.7	(3.9)	15.8	(2.1)	5.0	(1.2)	18.0	(8.0)	38.5	(8.1)	3.0	(1.2)	1.1	(0.5)
bulk paste	0	15.7		8.7		2.7		2.6		68.0		0.8		1.3	
	10	10.1		7.1		2.7		4.7		67.7		2.6		5.1	
	45	13.0	(3.7)	8.2	(0.9)	2.9	(1.2)	6.4	(2.5)	60.3	(1.4)	1.6	(0.5)	7.6	(2.4)
	90	13.7		8.7		3.8		6.6		60.0		1.6		5.6	
	120	13.6		12.5		4.2		4.7		58.4		0.7		6.0	

The values at 0 minutes of hydration correspond to the unhydrated cement. All values shown are the percentage of crystalline material analyzed. The standard deviation is shown in parenthesis.

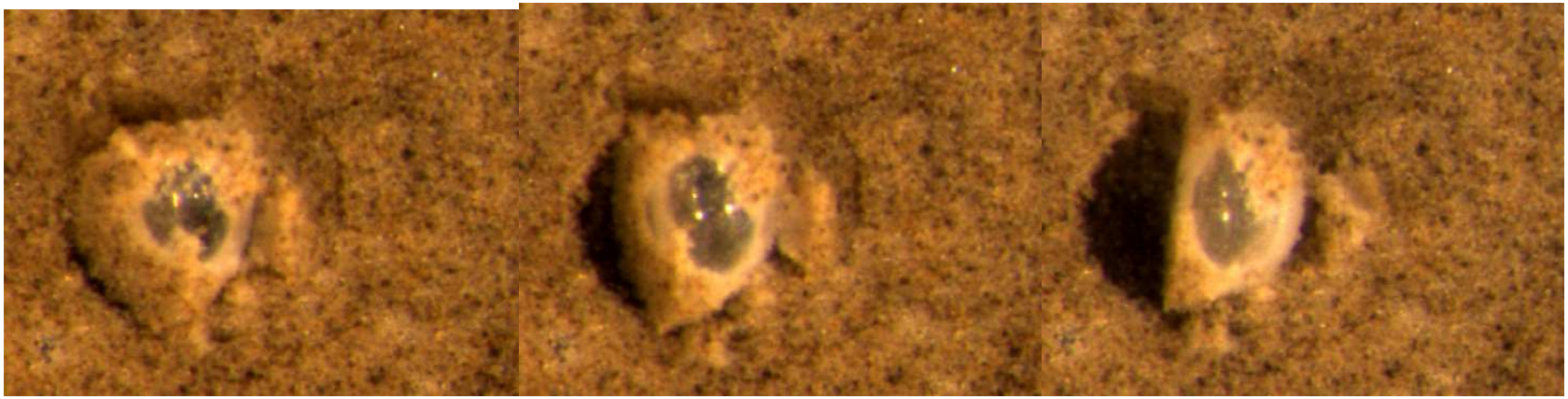


The detail cross-section is at two time intervals. The time is displayed in minutes after initial hydration/time after the bottle was placed on its side.

Fig. 7.1 – The experimental setup for the physical testing showing the orientation of bottle, stereoscope, and point light source.

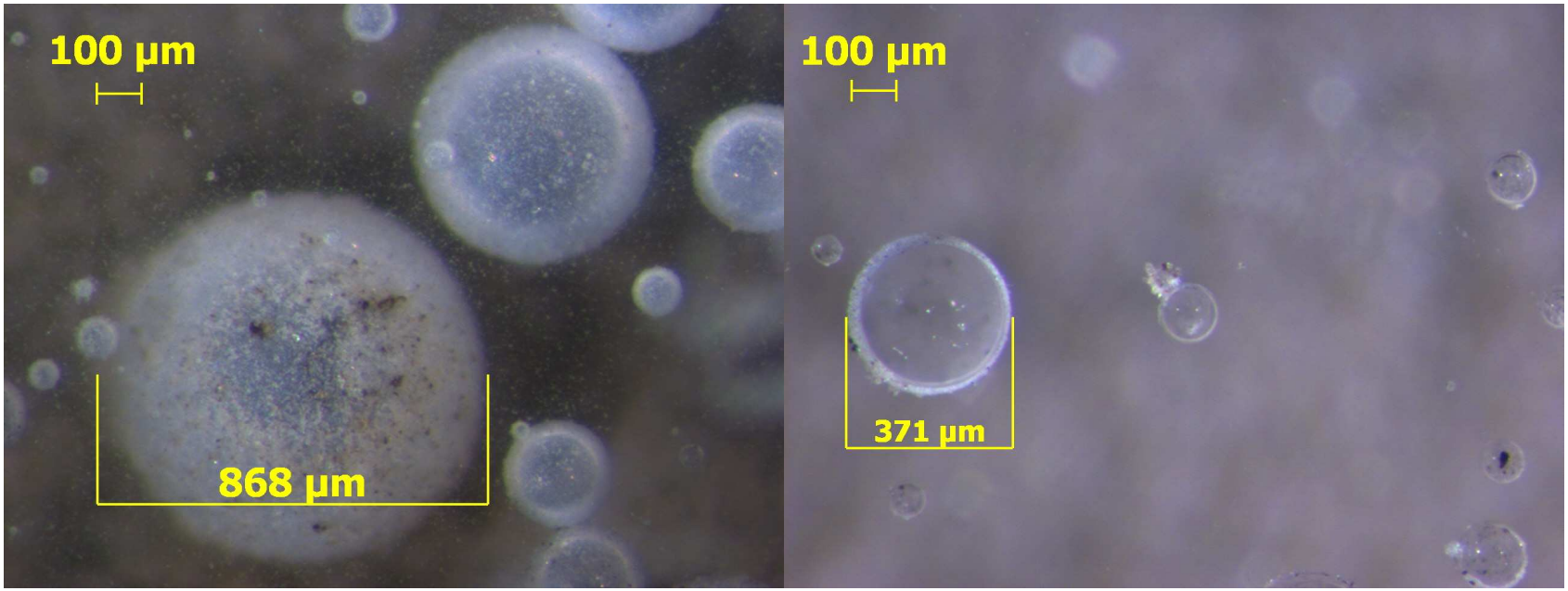


7.2A – 10 minutes 7.2B – 11.3 minutes 7.2C – 12.5 minutes



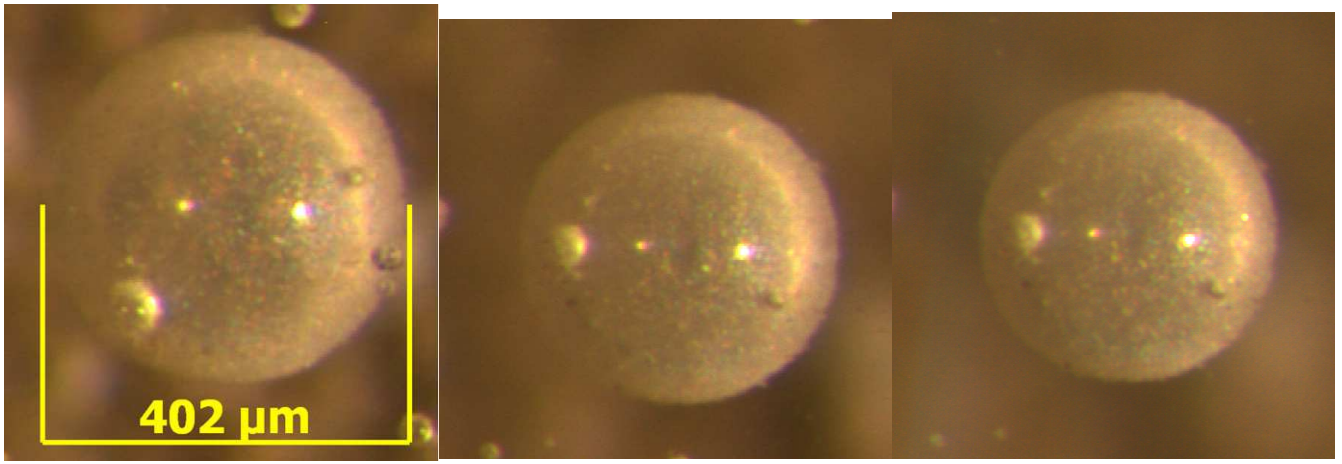
7.2D – 13.3 minutes 7.2E – 13.5 minutes 7.2F – 14.8 minutes

Fig. 7.2 – An air-entrained void is shown emerging from a cement paste surface due to buoyancy with cement grains attached. The paste was made with 48 mL/100 kg of cm of a wood rosin AEA.

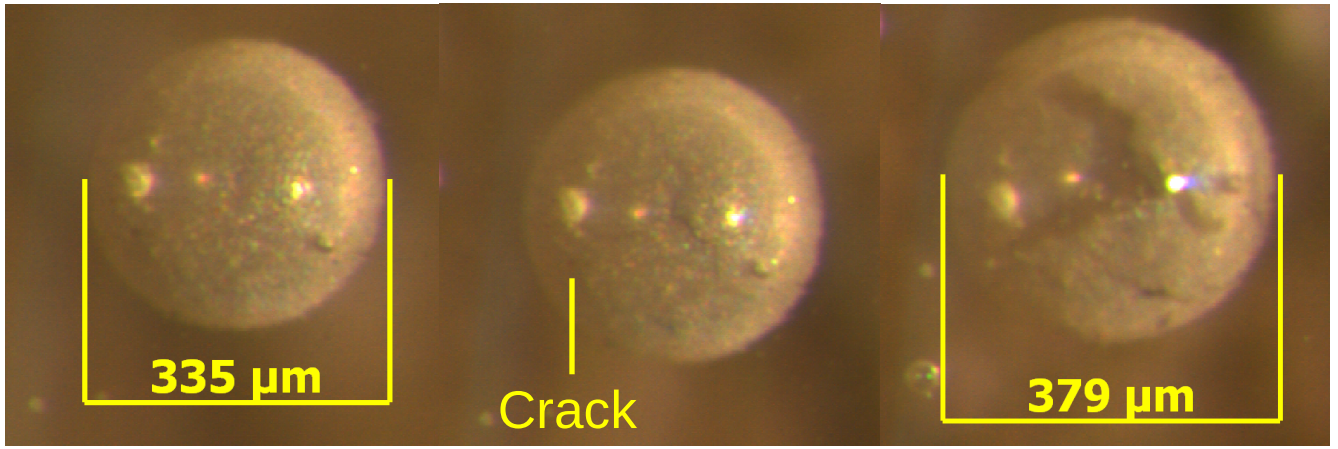


7.3A 7.3B

Fig. 7.3 – A. Air-entrained void (48 mL/100 kg of cm wood rosin AEA) after 45 minutes of hydration, B. Non air-entrained voids after 45 minutes of hydration.

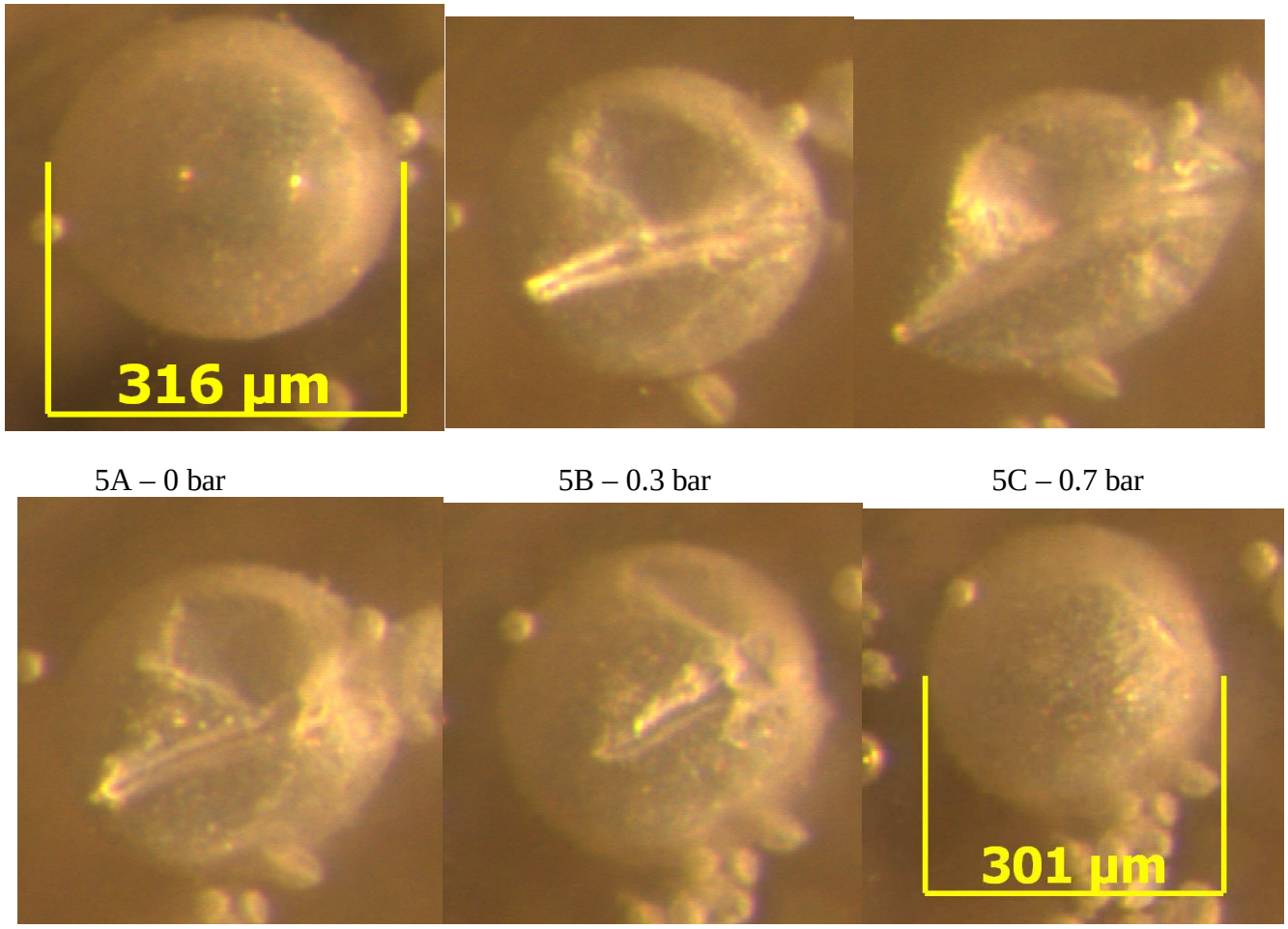


7.4A – 0 bar 7.4B – 0.2 bar 7.4C – 0.5 bar



7.4D – 0.7 bar 7.4E – 0.3 bar 7.4F – 0 bar

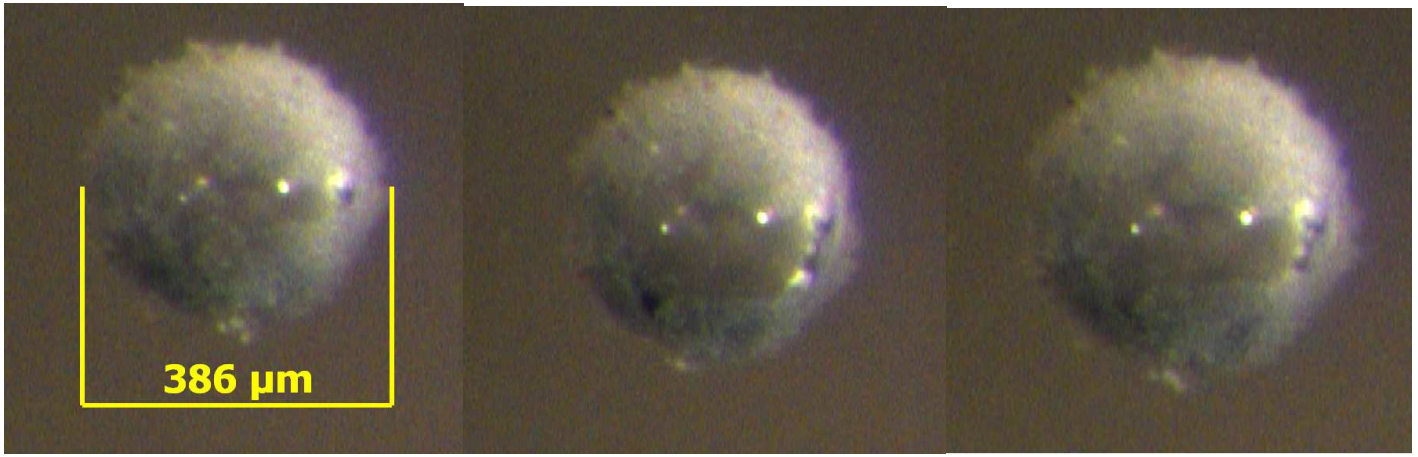
Fig. 7.4 – The response of a mixture containing 26 mL/100 kg cm of Vinsol resin and 81 mL/100 kg of normal range water reducer subjected to a pressure 0.7 bar above atmospheric and then returned back to atmospheric pressure.



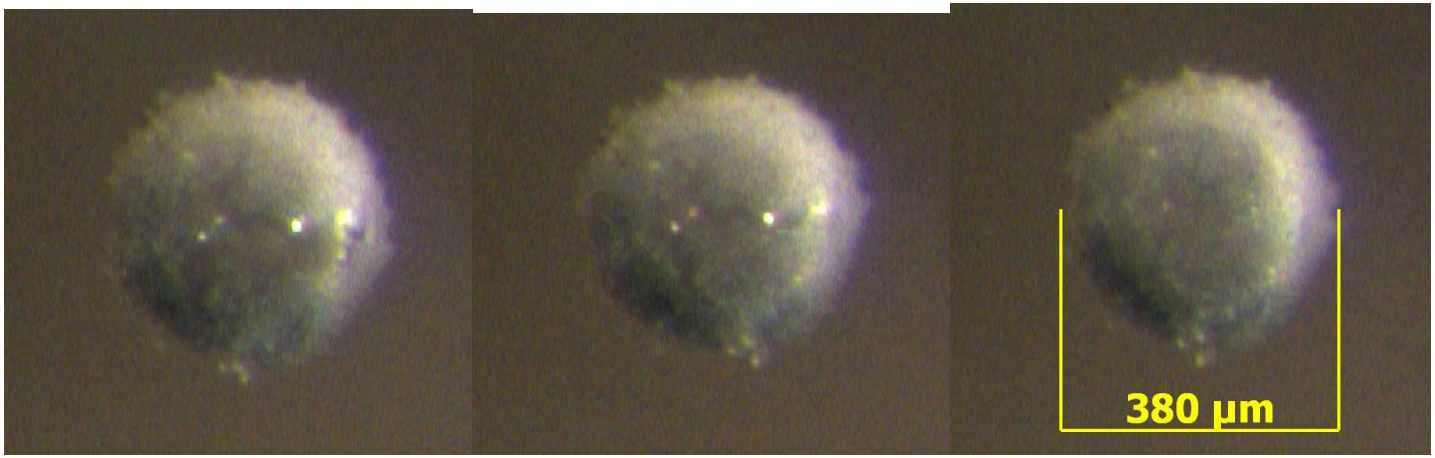
5A – 0 bar 5B – 0.3 bar 5C – 0.7 bar

7.5D – 0.2 bar 7.5E - 0.1 bar 7.5F – 0 bar

Fig. 7.5 - The response of an air-entrained void in a mixture (47 mL/100 kg of cm of synthetic AEA and 81 mL/100 kg of normal range water reducer) subjected to a pressure 0.7 bar above atmospheric and then returned back to atmospheric pressure.



7.6A – 0.8 hours 7.6B – 1.2 hours 7.6C – 3.6 hours



7.6D – 3.9 hours 7.6E – 4.8 hours 7.6F – 6.4 hours

Fig. 7.6 – A void in bleed water above a cement paste (48 mL/100 kg of cm of a wood rosin AEA) was subjected to a pressure 0.7 bar above atmospheric and then returned back to atmospheric pressure.

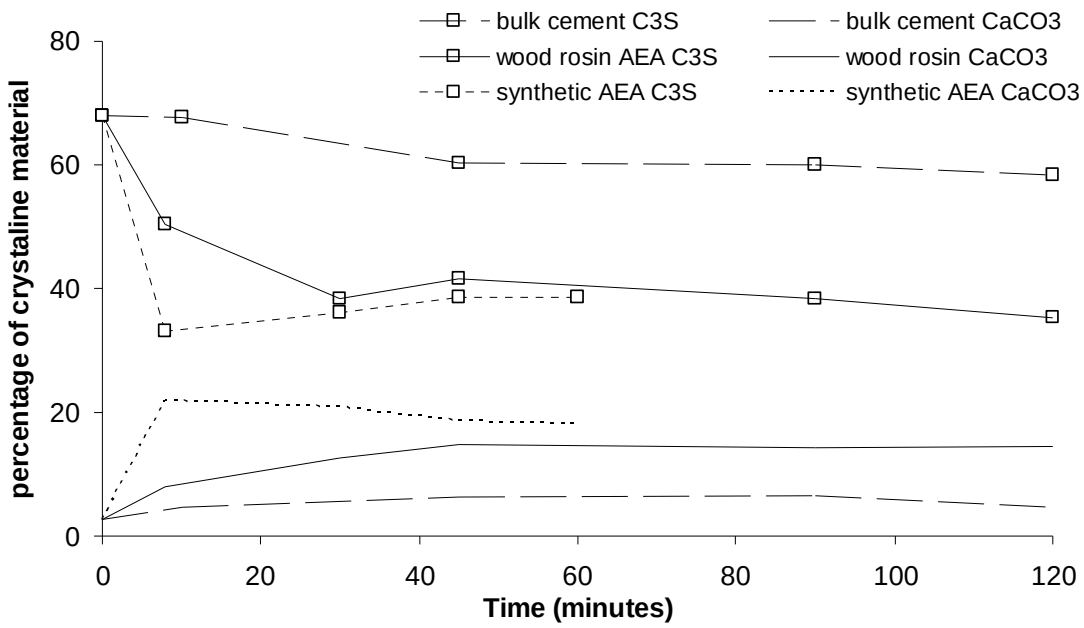
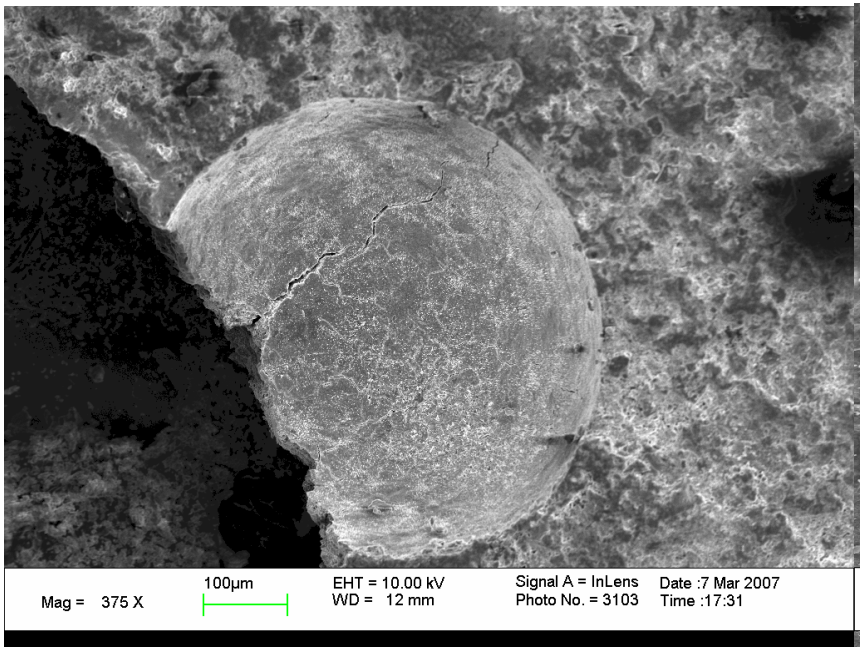
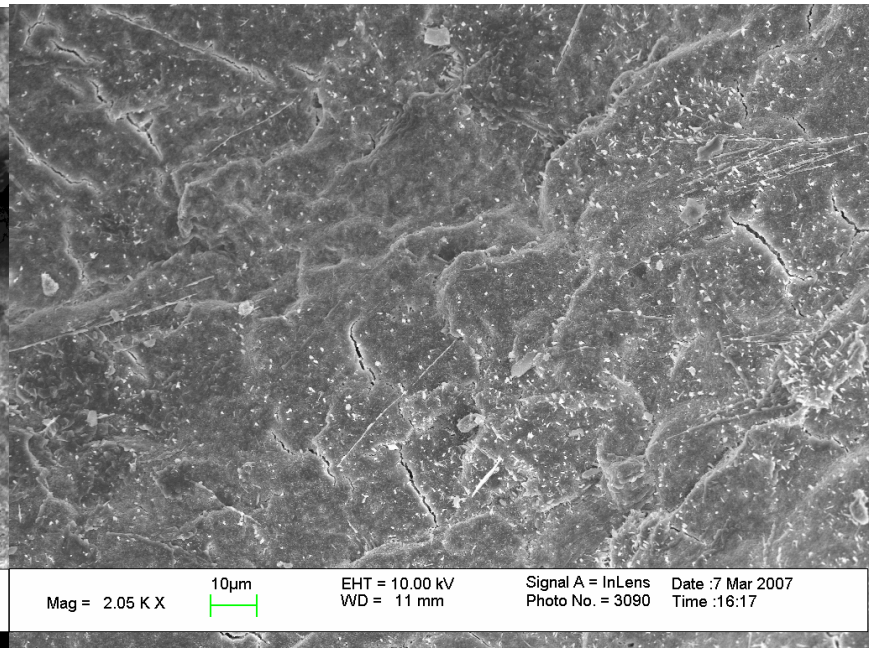


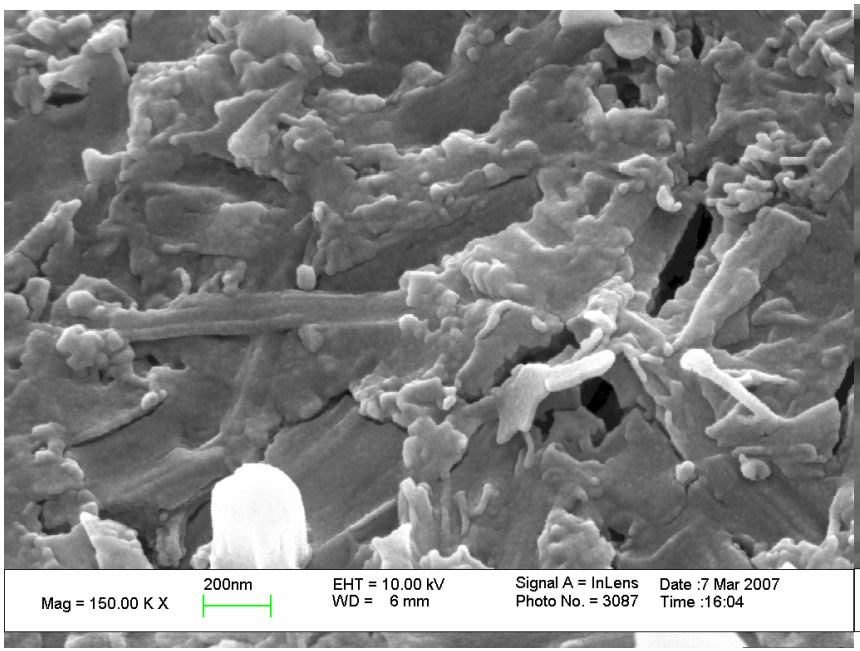
Fig. 7.7 – Change in C_3S and $CaCO_3$ content with time is shown for the bulk cement paste and the air-void shells created with wood rosin and synthetic AEAs

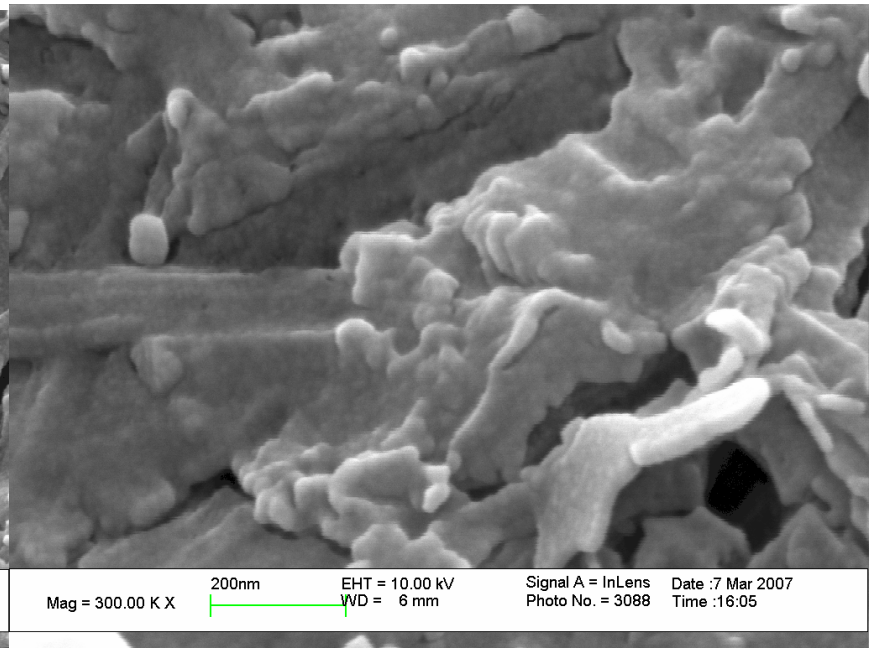

Mag = 375 X
100µm
EHT = 10.00 kV
WD = 12 mm
Signal A = InLens
Photo No. = 3103
Date :7 Mar 2007
Time :17:31

7.8A


Mag = 2.05 K X
10µm
EHT = 10.00 kV
WD = 11 mm
Signal A = InLens
Photo No. = 3090
Date :7 Mar 2007
Time :16:17

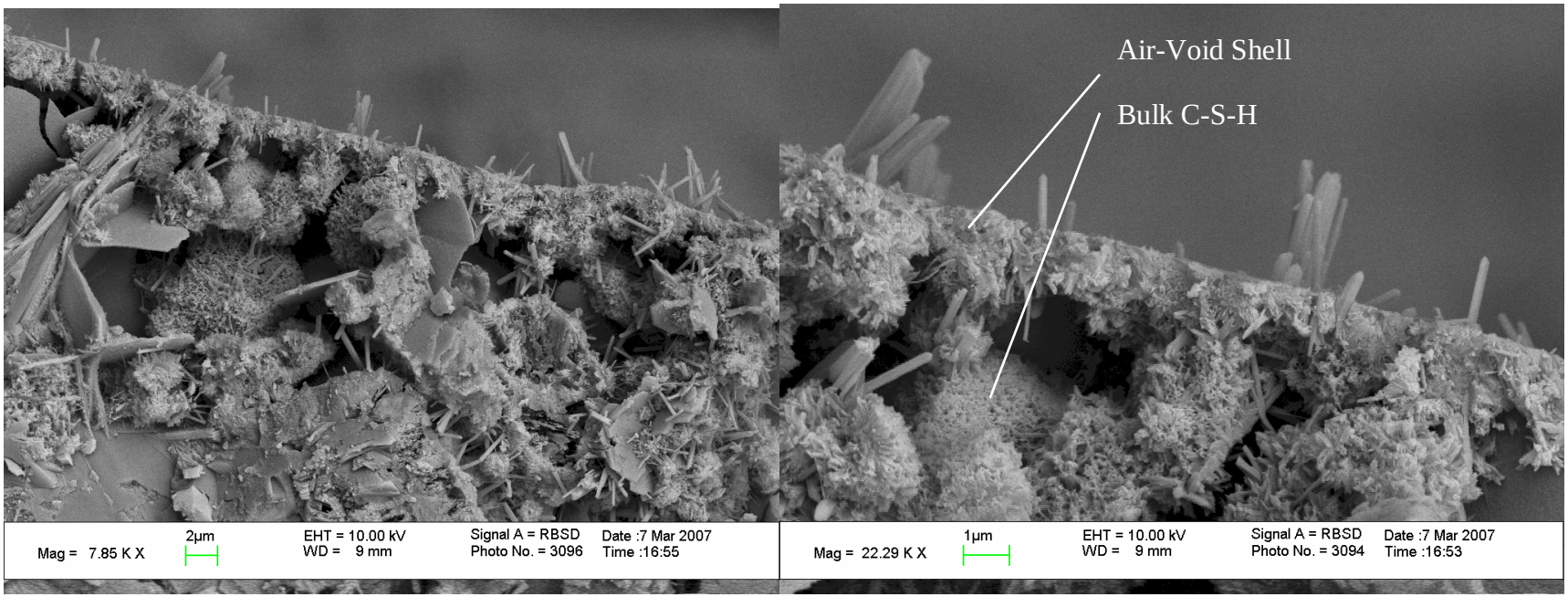
7.8B





7.8C 7.8D

Fig. 7.8 - SEM image of an air-entrained void from a mixture containing a wood rosin AEA at 48 mL/100 kg of cement that was allowed to hydrate for 60 days before examination. An overview of the void is shown in Fig. 7.8A. The surface of the air-void is shown in Fig. 7.8B. Fig. 7.8C and 7.8D show the voids surface under increased magnification.



7.9A 7.9B

Fig. 7.9 – A SEM image of the interface between the air-void in Fig. 7.8 and the bulk paste. In Fig. 7.9B a close up is shown of Fig. 7.9A.

Chapter 8: Conclusions

The research presented in this dissertation provides a multi-scale approach to achieving a better understanding of the challenges of entraining and stabilizing air-voids in concrete. While several questions remain, it is hoped that the information in this dissertation provides some new insight into air-entrained concrete, an amazingly complicated and useful building material.

The main conclusions of this dissertation are:

8.1 Investigation of Air-Entraining Admixture Dosage in Fly Ash Concrete

- Fly ashes from power plants that have been modified with low-NOx burners generally led to increases in AEA demand in laboratory testing, and this observation generally agrees with the field reports of increased AEA dosages during this time period. However, it cannot be said with certainty is that the installation of the low NOx burners, per se, is responsible for these observed changes in the ash.
- Loss-on-ignition (LOI) (ASTM C 311) measurements did not correlate with the AEA demand in concrete for most of the fly ashes studied in this project.
- The foam index test used in this study showed a satisfactory correlation to the AEA demand in concrete; however, it was unable to differentiate fly ashes with low AEA demand (less than 60 ml AEA/100 kg cm for 6% air in fresh concrete air tests)
- Limited results suggest that surface area, as indicated by nitrogen absorption using Brunauer-Emmet-Teller (BET) analysis, is a good indicator of AEA demand, especially for ashes with highly active carbon.

- BET surface area measurements were taken before and after igniting the ash (using LOI procedure), with a significant decrease in surface area measured on the ignited samples (compared to the as-received ashes). These ignited ashes were then found to respond better to AEAs in foam index testing, suggesting that the loss of carbon (along with other impurities/organics) and the associated surface area contributed to AEA demand

8.2 EVALUATION AND IMPROVEMENT OF THE ASTM C 311 AIR-ENTRAINMENT OF MORTAR WITH FLY ASH TEST

- For the work performed under this project, an average percent difference of 48% was measured for the mortar air test specified in ASTM C 311. This large variation was found to be a result of the fixed flow rate and air content of the mortar investigated.
- The ASTM C 311 test was modified to remove the iterations in the test and to reduce the variation. This was done by fixing the water content and AEA dosage in the test. This test has been shown to have a satisfactory variability but the correlation of the testing results to concrete could be improved.

8.3 DETERMINING THE AIR-ENTRAINING ADMIXTURE DOSAGE RESPONSE FROM A SINGLE CONCRETE MIXTURE

- A method was presented to produce an AEA dosage response curve for a given fly ash/AEA combination using only using a single mixture. The method was then compared to the standard test for AEA dosage response that uses several sequential mixtures and the results were found to be closely comparable for air contents up to 7%.
- The water reducer (WR) used in this study was shown to reduce the AEA demand (to achieve a target air content) as the WR dosage was increased.
- A sacrificial surfactant that is applied to fly ash with high AEA demand can decrease the AEA demand of fly ash concrete.

- The mixing temperature had a larger impact on the AEA demand of a fly ash treated with a sacrificial surfactant than on the AEA demand of the other fly ash mixtures investigated.
- As the percent fly ash replacement increased in a concrete mixture, the AEA demand in fly ash concrete decreased if the AEA demand of the fly ash was low or increased if the AEA demand of the fly ash was high. This increase occurred in a nonlinear fashion.
- The AEA demand of fly ash treated with a sacrificial surfactant did not change as the percent fly ash replacement increased.
- A wood rosin AEA is the most sensitive of the AEAs examined to a fly ash with a high AEA demand in concrete.

8.4 INVESTIGATION OF THE FROST RESISTANCE OF CONCRETE THROUGH MEASUREMENT OF FRESH AND HARDENED PROPERTIES, AND RESISTANCE TO RAPID FREEZING AND THAWING CYCLES

- Based on a small data set of mixtures with a similar mixture design but different air content as determined by ASTM C 231 (pressure method), the commercially available Air-Void Analyzer (AVA) was determined to have significant variability between two measurements examined from the same mixture. Significant differences were found between air-void parameters obtained from the hardened air-void analysis and the AVA.
- It was found that concrete mixtures with an air content greater than or equal to 5% was generally frost resistant (using ASTM C 666). Some mixtures with lower air contents were not frost resistant, especially mixtures containing high amounts of WR (and lower AEA dosages), mixtures with porous aggregates for which the aggregate correction factors were not applied, or mixtures containing a fly ash treated with a sacrificial surfactant. However, none of the variables listed previously were investigated in combination.

- For mixtures with relatively low air contents (e.g., less than 4.5% air) and containing a fly ash treated with a sacrificial surfactant, a coarsening of the air-void system was observed, manifested in an increase in the average chord length of air voids. However, once the air content was increased to 5% or above, satisfactory frost resistance was obtained.

8.5 OBSERVATIONS OF AIR BUBBLES FROM FRESH CEMENT PASTE

- An opaque "shell" was observed on the exterior of air bubbles that had escaped from air entrained paste. The appearance of the shell changed as different AEA admixtures were used.
- In these experiments with bubbles in bleed water, bubbles with an opaque shell appeared to resist coalescence, whereas translucent-to-transparent bubbles coalesced readily. Similarly, the shell appeared to take on structural properties such as stiffness, resistance to deformation, and eventual cracking. The role of these properties in stabilizing air bubbles within cement paste has not been identified.
- When the shell appeared to be fully intact over observable portions of the bubble surface, the diameter of the bubbles did not change with time for the conditions of setup #2. When a readily discernable shell was not present as in the specimen of non air-entrained paste in setup #2, the diameter of the air bubbles was observed to change with time. Likewise, of those bubbles with a readily observed shell, only those that had cracked changed diameter with time.
- In pressurized experiments shown in setup #3 it was observed that the air-bubble shell was damaged during depressurization from 0.7 bar to atmospheric pressure. This may be important in construction applications in which the concrete pressure is increased and decreased. It is not known, however, whether the experimental observations made here under a relatively mild and slow pressure change apply

equally to the much higher pressure differences and rates of pressure change experienced in concrete pumping, for example.

- A single shell-covered bubble that had escaped from air-entrained paste was observed to decrease in volume under pressure precisely as would be predicted by Boyle's Law, with no apparent influence of the shell.

- If a water-filled gap does exist between the air-void shell and the surrounding paste as observed by others in concrete (Rashad and Williamson, 1991A; Rashad and Williamson, 1991B; Corr et al., 2002), then it seems plausible that gas interchange could occur between air-voids whose shells were either inadequate or damaged. This interchange could lead to a decrease in volume of the smaller bubbles and an increase in volume of the larger bubbles as observed in the experimental work in this paper. This change in void volume would ultimately lead to a higher overall air content in the mixture as the gas is under a lower pressure in the larger air-voids than the small; therefore, the air would take up a larger volume on transfer as first suggested by Mielenz et al. (1958A). The above explanation is based on observations of air-void behavior in the bleed water of cement paste and has not been proven in concrete mixtures.

8.6 THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SHELL OF AIR-ENTRAINED BUBBLES IN CEMENT PASTE

- It has been shown that there is a strong adhesion between cement particles and air-voids beginning at the first minutes of hydration.
- It appears that there is a large difference in transparency between the air-entrained and non air-entrained voids as well as a difference in the ability of the voids to resist size changes with time.
- There is a significant difference in performance between the resulting shells with different AEA admixtures when the fluid pressure surrounding voids is increased

and then decreased again to atmospheric pressure. Voids made with synthetic AEA sustain no permanent damage, while voids made with Vinsol resin and wood rosin crack on depressurization.

- The cracks in a wood rosin void shell were observed to self-heal.
- The amount of C_3S present in the air-void shell is lower than in the original unhydrated cement and the bulk paste This effect may be due to delays in the induction period for the C_3S particles at the air-void surface.
- The increase in $CaCO_3$ in the air-void shell in the first two hours of testing may be an artifact of the sample preparation technique as it was not observed in the SEM analysis of the 60 day old air-void shell.
- The rate of C_3S decrease and $CaCO_3$ increase is faster for synthetic AEA than for wood rosin AEA. It is likely that this difference in hydration rate is related to the difference in behavior of the air-void shells of the different AEAs.
- SEM observations and EDXA of the air-voids in the 60-day-old cement paste showed that the surface of the air-void seems to be predominately made up of a C-S-H phase that is of a different stoichiometry than that found in the C-S-H of the bulk paste as the ratio of the calcium-to-silicon of the air-void shell is around 1.1 compared to 1.5 as found in the bulk paste.

8.7 RECOMMENDATIONS

One of the major goals of this research project was to recommend test methods that have the ability to determine the AEA demand of fly ash in concrete. One criterion of these methods was for them to be simple and applicable in the field as well as in a quality control laboratory. While a large amount of work was completed on this task at Cornell University including: investigations of several novel and existing test methods and the mechanistic behavior of the impact of fly ash on the AEA demand of concrete, recommendations will be made only based on the work contained in this dissertation.

However, the findings from Cornell University will be combined when presenting the final deliverables to TxDOT.

- The foam index test shows the most promise of the tests investigated. This test does not require any complicated equipment and has been shown at least for the mixture proportions investigated to provide a reasonable prediction of the AEA demand of the fly ash in concrete. One problem with this test is that the results are based on human subjectivity in the mixing and evaluation. This subjectivity may be overcome if the tests are completed by experienced technician. More data are presented in the dissertation of Nathan Harris at Cornell University. (Harris, 2007)
- The modified mortar air test developed in this dissertation showed a lower variability then the current ASTM C 311 mortar test and requires significantly fewer mixtures to be created. This test is useful in that it does not rely on human subjectivity for mixing or evaluation. However, this test requires somewhat specialized equipment and the correlation to the performance of the concrete mixtures was better for the foam index test.
- The BET nitrogen surface area testing, for the limited data set presented, showed a satisfactory ability to examine the AEA demand of a fly ash in concrete. However, this test requires very expensive equipment. Additional work completed at Cornell University should be consulted before recommending this test. However, the high expense for the equipment does not meet the requirements set by TxDOT.
- The LOI test showed little or no correlation to the AEA demand of a fly ash in concrete for the fly ashes evaluated in this particular study and requires specialized equipment. While this test is a standard in the concrete industry it is not recommended to evaluate the AEA demand of fly ashes in this study.

The previously mentioned tests have been shown to be useful when examining the AEA demand of fly ash in concrete. However, for the mixtures investigated, a large number of factors can impact the ability to entrain air in concrete. Because these previously mentioned tests were completed on simplified systems or measured physical properties of the fly ash they are unable, and should not be expected, to describe all of the different combinations that may impact the ability to entrain air in concrete. However, the best method to investigate the impact of different mixture ingredients on the ability to entrain air in concrete is to create a trial concrete mixture. In the past this would have required the creation of several mixtures that may have unintentional differences that impact the ability to entrain air in concrete. However, the methodology outlined in this dissertation allows the impact on the AEA demand of these variables to reliably be investigated from a single concrete mixture. While this test is not as simple as the ones described previously and does not satisfy the initial requirements set by the problem statement it does provide a direct measurement of the impact of different mixture ingredients on the ability to entrain air of the mixture in question.

A number of variables were investigated which have the ability to impact the AEA demand and resulting air-void system in concrete. It has been shown that in a limited number of tests that the following variables may not provide satisfactory frost durability at air contents lower then 4.5% as determined by the ASTM C 231 (pressure method). Because of this it is recommended that an air content of at least 5% is provided in a hardened concrete that is desired to be resistant to freeze-thaw damage, as this was shown as the threshold air content that performance was satisfactory. However, it should be said that no combination of these variables were investigated and that the results of an investigation may yield different recommendations. It would be prudent to require that a minimum dosage of AEA be required in a concrete mixture. One possibility is to utilize the manufacturer's minimum suggested dosage until other limits can be established.

The Air Void Analyzer was shown to have a significant difference between the air-void parameters in the hardened air-void analysis and for this reason is not recommended to be utilized to evaluate the air-void system in concrete as a construction specification until a better understanding is obtained of how the measurements of the machine correspond to the air-void system in the sampled concrete.

While no evidence is presented in this dissertation of the air-void system changing with time in concrete, optical observations of the air-void system in pastes suggest that it is possible for air-voids to change in size with time as first suggested by Mielenz et al. (1958A). These observations suggest that the hydration shell formed around air-entrained voids may be important to the stability of the air-void system. This shell was shown to form in concrete with AEA and not shown in concrete without AEA. The relevance of these observations to concrete deserves more attention. However, these observations reinforce the need for the quality control testing of the air content in concrete to be completed as close to the point of placement as is feasible in order to best measure the in-place air content.

8.8 RESEARCH NEEDS

This project was one that was quite ambitious in scope. Work in this dissertation provided new information not currently in the state of the art on testing methods, performance of different ingredients in concrete, the characteristics of the air-void shell, and the chemical properties of this shell. It is unfortunate but inevitable that some research needs still remain. The following is a list of the most pressing research needs.

- Different combinations of water reducer dosage, sacrificial surfactant, and aggregates with different correction factors should be investigated that are typically used in concrete construction to investigate the air-void systems produced with different air contents.
- The vast majority of the mixtures performed for this research focused on a concrete mixture that would be typical of a bridge deck mixture. Other mixture

proportions representative of other applications should be investigated to monitor the impact of different variables on the resulting air-void content and distribution.

- A subset of the most critical mixture combinations from the previous recommendations should be investigated in a set of full scale mixtures created in a ready-mix concrete plant and the resulting air content and air-void distribution should be evaluated.
- A survey of the aggregate correction factor of aggregates should be completed in locations where freeze-thaw durability is specified. Different moisture contents of these aggregates should also be investigated to determine the impact on the accuracy of the ASTM C 231 pressure method to measurements made on hardened concrete.
- A detailed study is needed to examine how the air-void shells impact the change in the air-void distribution in concrete.
- More work is needed to further characterize the chemistry of the air-void shells. The focus of this research is to isolate several of the variables and develop a less intrusive technique to separate the air-voids from the paste and compare the results to previous testing. Also more work is needed with different AEAs to understand why they show distinctly different physical properties.
- The overall findings in this dissertation need to be combined with the findings from Cornell in order to compare the specific research on the simple test methods and fly ash properties to overall performance in concrete.

Appendix A: Hardened Air-Void Analysis Parameters

A.1 INTRODUCTION

This appendix presents a study on the effects of two parameters, threshold value and analysis length, on the results of an automated hardened air-void analysis completed with the RapidAir457 (Concrete Experts International). These are two parameters for which little or no previous guidance exists on how they can affect the results. Therefore some simple tests were performed and this appendix presents the results and gives the justification for the values and methodology used in this dissertation.

A.1.1 Length of Linear Traverse

One advantage of utilizing an automated system to analyze the surface of a lapped concrete specimen is that certain parameters can be adjusted to provide a more thorough analysis with very little increase in time; this type of testing would be too costly and time prohibitive to be done regularly with a human analysis. One parameter that is easily adjusted is the length of the traverse in the analysis, as the RapidAir457 has a feature that permits multiple linear traverse lines to be used to simultaneously investigate the viewing area. This is useful as it allows the camera to travel the typical distance of one linear traverse while completing an actual analysis equal to the number of lines chosen multiplied by the length of traverse. For example if the user chooses to run three linear traverse lines simultaneously, then the actual traverse length of the specimen will be equal to three times the length the camera travels over the specimen. Therefore, multiple traverse lengths can be covered in the same amount of time it would take for the camera to complete a single linear traverse. This feature could also be used to lower the time needed to complete a single linear traverse as multiple traverse lines could be utilized while covering a shorter distance. The reduction in distance needed to complete a typical

ASTM C 457 traverse length will be proportional to the number of simultaneous traverse lines used.

A.1.2 Threshold Value

As described in Appendix B and Chapter 4 the surfaces of the polished concrete specimens must be colored black and filled with a white powder once the polishing is complete in order for it to be analyzed with the automated hardened air-void analysis. The operator of the automated analysis system must choose a "threshold value" for the sample. This parameter sets the definition of what is considered black and white by deciding a shade of gray as the point of differentiation between the two in the analysis. Currently, there is no standard method to choose this parameter and it is the responsibility of the user to use his or her judgment to decide which value to use for the specimen. Fig. A1 shows several screen shots of the same area of analysis with different threshold values. The raw black and white image is also provided for comparison. As the threshold value is decreased the amount of white is reduced on the screen and hence the amount of apparent air-voids. In the RapidAir457 manual and in the training provided by the equipment supplier, on how to select this number. When asked about this in the training for the system it was suggested that "The user[s] should choose the threshold value that they think best represents the sample" (Jakobsen, 2005). Since this is a possible source of variability in the test it was decided to be investigated further.

A.2 EXPERIMENTAL METHODS

A.2.1 Linear Traverse

Five specimens with hardened air contents between 2.6% and 7% and with a nominal aggregate size of 25 mm were compared in the automated hardened air void analysis with traverse lengths and area to be investigated specified in ASTM C 457. Another analysis was completed where the camera started in the same position and covered the same traverse path but three traverse lines were utilized. This allowed a

distance three times the amount specified in ASTM C 457 to be covered. Both of these analyses were started in the same location and traversed the specimen in the same path.

A.2.2 Threshold Value

As a part of the computer interface with the RapidAir 457, a value is provided that reports to the user the amount of white (estimated air content) that is currently in the analysis window. This value will change as one adjusts the threshold value as discussed previously and shown in Fig. A.1. In order to investigate how the threshold value affects the amount of air determined in the viewing window, a test was completed where two different spots on the sample surface were examined under varying threshold values and the resulting percentage of white was recorded.

Next a comparison was made between threshold values of three different users from twelve different locations on the surface of a specimen. These locations were chosen so that they would be at approximately 12 equal spaced locations on the surface of the specimen. Each user chose the threshold value in private and the results were not shared between users. The only instruction provided to the user was to "choose the threshold value that best represents the sample.

Finally, three samples were analyzed with different threshold values to investigate the impact on the results of the automated analysis. The same sample utilized in the survey for the three different users was analyzed utilizing the average threshold values from the survey. All of the samples used the same traverse length and path on each sample and so the threshold value is the only variable being investigated. These specimens were chosen as they had air contents which consistently provided air void parameters that were very close to the common recommended values for air-void parameters in hardened concrete (spacing factor 0.200 mm and specific surface 24 mm^2/mm^3). Therefore, it seemed important to investigate how these specimens were impacted by changes in threshold value.

A.3 RESULTS AND DISCUSSION

A.3.1 Length of Linear Traverse

Table A.1 presents the results of the hardened air-void analysis for traverse lengths as required by linear traverse analysis for ASTM C 457 and for the larger length with the RapidAir457. One significant difference between the results is the number of voids analyzed with the longer traverse length. This would suggest that since a larger number of voids have been inspected then a more representative analysis of the air-void parameters should be provided. For the majority of the comparisons shown in Table A.1 the results are similar. The samples that had the lowest air contents showed very similar results between the typical and extended traverse length. However, as the air content of the mixtures increased, then there was more of a difference between analysis results. The air content seemed to be the parameter that was most sensitive to the hardened air-void analysis. It would be expected, but not proven herein, that the precision of the longer traverse lengths to the actual air content in the mixture would be better compared to the precision of the shorter traverse lengths.

A.3.2 Threshold Value

The values for the percentage white displayed at two different places on a sample's surface is shown in Fig. A.2. The results from this examination suggest that the percentage white displayed on the screen versus the threshold value is an S shaped curve. This curve shows a large change in the percentage of white displayed at the extremes of the curve and a linear portion between these two values. This plot suggests that the amount of white detected by the analysis window should change linearly between threshold values chosen away from the extremes of the threshold values.

The individual results and average threshold values are reported in Table A.2 for the three different users. As can be seen from the data the average threshold for users 2 and 3 were essentially the same and the average value for user 1 was 15% less. When

interviewed after the test, users 2 and 3 both said that they adjusted the threshold value so that the analysis window best matched the raw data image. User 1 said that he changed the threshold value to best replicate all of the small air voids and did not attempt to make the entire image represent the raw image. These data suggest that when different users have the same opinion about the way something should look then the average results were similar for 12 different observations. However, different opinions of users can lead to different threshold values chosen for a sample.

In Table A.3 the results of three different samples are compared with different threshold values and the different results from the hardened air-void analysis. In the table the percentage change is reported in parenthesis for each one of the air-void parameters but also for the change in the threshold value. All of the threshold values were in the central portion of the characteristic "S" shape shown in Fig. A.2. Also, the threshold value in which the other two analyses are compared to those chosen by user 2 using the same methodology used in the survey. The first specimen shown in the table was the same one used in the previous comparison of threshold values for three different users. The low threshold value for the first sample was chosen to match the result of user 1. The high threshold value was chosen to be the same percent difference between the results of the two users. The results suggest that none of the air-void parameters change at a larger percentage rate than the threshold change. Of all the parameters investigated it appears the void frequency is the most affected by the changes in threshold value. This parameter seems to change at a similar percentage as the threshold value. The air content and specific surface seem to change at a percentage rate that is approximately 50% of the change in the threshold value and change in the specific surface seems to be approximately 25% of the change in the threshold value. It should be noted that in all of these mixtures the paste to air ratio was determined to be larger than 4.342 and so the following equation was used to calculate the spacing factor as determined by ASTM C 457:

$$\bar{L}=\frac{3}{\alpha}\left[1.4\left(1+\frac{p}{A}\right)^{1/3}-1\right]$$

Equation 1

This indicates that the offset of the changes in the specific surface and the paste to air ratio consistently offsets to provide a spacing factor that is approximately 50% of the threshold value change. These results may be different if a different sample preparation technique, paste content, or if a different range of threshold values were chosen.

A.4 CONCLUSION

This appendix presented the results from an investigation of how the traverse length and the threshold value impacted the results of the RapidAir457 analysis.

It was determined that the longer traverse length should be used as it investigated a large number of air-voids and therefore, should provide a better characterization of the hardened air-void system while having a minimum impact on the amount of time required to complete the analysis for that specimen.

For this study it was decided that the user should choose the threshold value by adjusting the analysis image until it best matches the raw image. Furthermore, in order to better characterize the threshold value for a specimen it was decided to take a threshold reading at 12 equally spaced locations on the surface of the sample, as this would provide a reasonable estimate of a threshold value for the entire specimen. From these 12 measurements the high and low values were removed and then the other ten were averaged. This was done because occasionally a location is analyzed in the paste where the amount of white is either very high or very low. In these locations it was determined that the threshold value chosen to match the analysis image to the raw image was significantly different than the other threshold values chosen. By removing the high and low values the probability for these areas to affect the average value is lowered. For the

hardened air-void analysis reported in this paper the threshold values used were between 158 and 174.

Table A.1 – Results from a hardened air-void analysis with different traverse lengths.

ASTM C 231 air content (%)	traverse length (mm)	air content (%)	hardened specific surface (mm^2/mm^3)	spacing factor (mm)	void freq. (mm^{-1})	avg. chord length (mm)	number of voids
2.8	2413	2.62	23.11	0.261	0.152	0.173	366
	7240	2.66	23.27	0.258	0.155	0.175	1321
3.3	2413	3.07	28.75	0.195	0.225	0.139	577
	7240	3.07	28.40	0.198	0.218	0.141	1576
4.4	2413	4.37	32.16	0.148	0.352	0.124	849
	7240	4.70	31.81	0.145	0.374	0.126	2706
5.2	2413	4.54	29.48	0.158	0.335	0.136	808
	7240	4.80	27.46	0.165	0.330	0.146	2387
7.8	2413	7.12	25.19	0.125	0.449	0.159	1083
	7240	6.71	26.19	0.128	0.439	0.153	3180

Table A.2 – Comparison of the threshold value chosen for three different users.

	User		
	1	2	3
	166	163	161
	135	166	150
	107	169	153
	120	166	153
	133	159	163
	197	160	157
	200	166	168
	102	170	170
	117	163	166
	126	153	169
	148	159	159
	122	163	188
Average	139	163	163

Table A.3 – A comparison of hardened air-void results with different threshold values.

ASTM C 231 air content (%)	hardened black/white threshold		air content (%)		specific surface (mm^2/mm^3)		spacing factor (mm)		void freq. (mm^{-1})		avg. chord length (mm)	
2.8	188	(+15.3)	2.48	(-6.8)	22.10	(-5.0)	0.280	(+8.7)	0.137	(-11.6)	0.181	(+3.4)
	163		2.66		23.27		0.258		0.155		0.175	
	138	(-15.3)	2.89	(+8.6)	24.57	(+5.6)	0.235	(-8.8)	0.178	(+14.8)	0.163	(-6.9)
3.3	175	(+11.5)	2.87	(-6.5)	27.57	(-2.9)	0.210	(+6.2)	0.198	(-9.2)	0.145	(+2.8)
	157		3.07		28.40		0.198		0.218		0.141	
	142	(-9.6)	3.27	(+6.5)	28.78	(+1.3)	0.190	(-4.1)	0.235	(+7.8)	0.139	(-1.4)
4.4	174	(+9.4)	4.32	(-8.1)	30.95	(-2.7)	0.153	(+5.9)	0.326	(-12.8)	0.131	(+4.0)
	159		4.7		31.81		0.145		0.374		0.126	
	142	(-10.7)	5.16	(+9.8)	32.67	(2.7)	0.135	(-6.7)	0.422	(+12.8)	0.122	(-3.2)

^ These values are not adjusted for the aggregate correction factor in order to best represent actual practice.

Numbers shown in parenthesis are the percent change in the parameter against the median threshold. For example between the first two rows in the table the threshold value was changed by 15.3% (from 163 to 188). This change in threshold value leads to a reduction in the air content by 6.8% (from 2.66% to 2.48%).

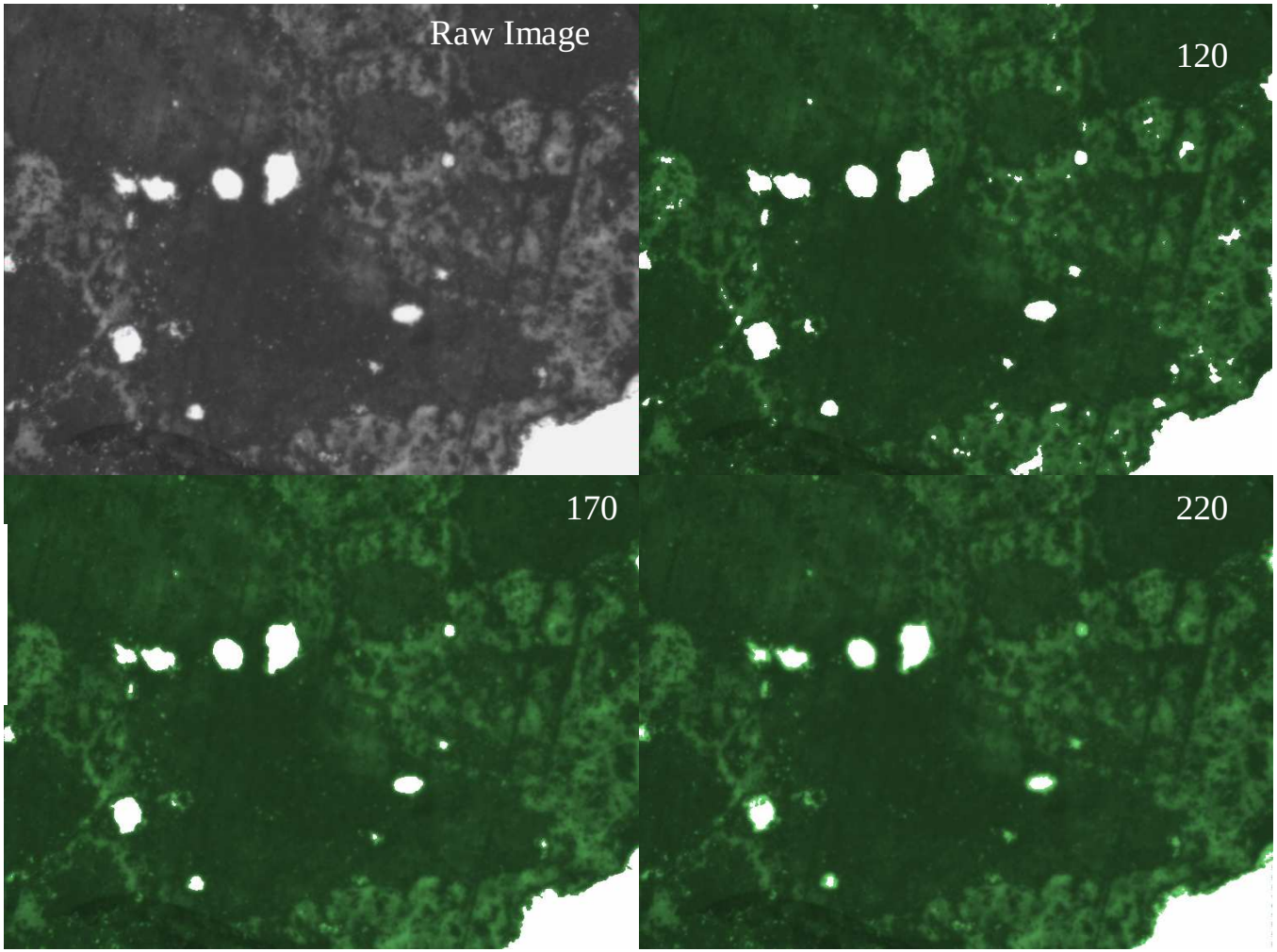


Fig. A.1 – A raw image and images with reported threshold values.

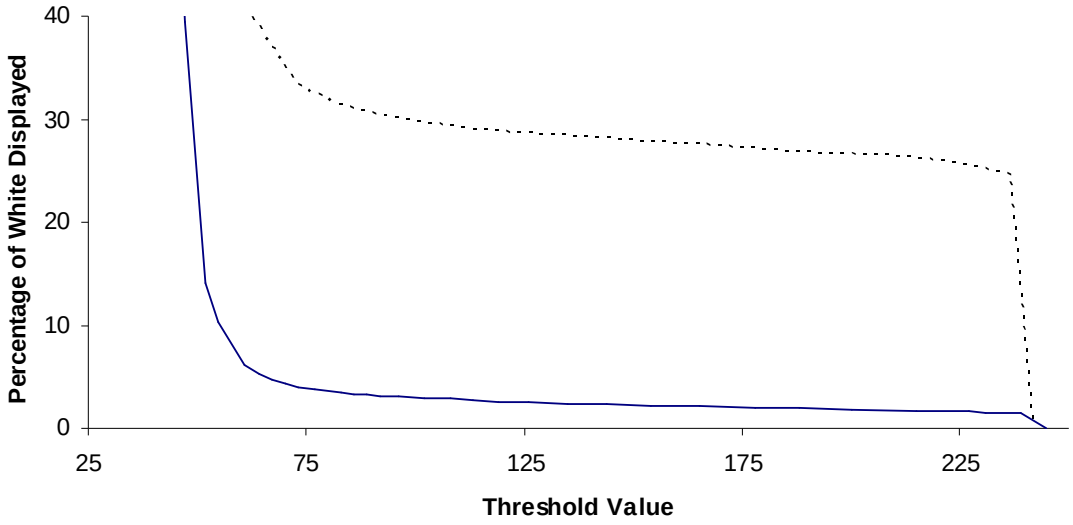


Fig. A.2 – Percentage white displayed on the screen as a function of the threshold value chosen for two different locations on the sample surface.

Appendix B: Sample Preparation for Hardened Air-Void Analysis

B.1 INTRODUCTION

This appendix contains a summary of the sample preparation techniques for the hardened air-void analysis. This appendix was created to give the reader a description of the methods utilized and to also serve as a guide to future researchers that may need to complete a hardened air-void analysis.

B.2 EQUIPMENT NEEDED FOR CONCRETE LAPPING (ASTM C 457)

Items needed:

- Construction crayon (yellow works best as it does not resemble paste or aggregate)
- Acetone
- Fine grained paint brush (for cleaning specimens)
- Paint brush (for applying lacquer)
- Polishng plates: nickel plated diamond discs with magnetic backing obtained from ASW diamond (www.aswdiamond.com). One should never use the felt discs to polish concrete.
- Lacquer (obtained from Sherwin-Williams Co. The manufacturer is Sheffield Bronze Paint Corporation. The product name is "Clear Lacquer.")

B.3 CUTTING THE SAMPLE

Place the wooden jig at the back of the automated Buehler Labpro 24 (lapidary) saw. Ensure that the concrete specimen is pushed snugly against the jig, and then tighten the clamp. After making the first cut, loosen the clamp, reposition the sample against the jig, retighten the clamp, and make the next cut. The jig setup has been designed to provide a pair of cuts that are parallel and leave a reasonable size sample (20 mm) to lap

and analyze with the RapidAir 457. After cutting the specimen wash the surface to remove any residue left behind from the saw. Pigeon and Pleu (1986) suggest leaving the cut specimens in water for a few days to help harden the surface. This technique was never tried.

B.4 CONCRETE LAPPING

Apply thinned lacquer (20% laquer/80% acetone) to the surface to strengthen the paste and to help reinforce the voids. Let the specimen sit for a minute or until dry. Be sure that the sample is left to dry in either a fume hood or a very well ventilated area. Use the construction crayon to mark a 10-mm x 10-mm grid on the surface to be analyzed.

Use the 80-grit pad to quickly remove any high spots or non uniform cuts made by the saw. Lap the sample until the crayon is completely removed. Care should be taken to insure that the surface is not preferentially lapped. This is easily checked by placing the long edge of a machinist's rule on the lapped surface of the specimen with a light behind it. The rule should be very flat and, if the lapped surface is not flat, one will see light between it and the rule. While some light will always get through this gap, large differences can be seen and the lapping technique adjusted to ensure that the sample surface is made flat. It is imperative that the sample be flat before leaving this grit size.

The time required to lap a specimen is determined by the condition of the lapping plate. New plates take about 30 seconds on this pad, and badly worn plates can take up to 30 minutes. The surface should be marked and lapped until all the crayon has been removed two times. Again, it is very important that the sample is plane before going on to the next step. Wash the sample well with the water hose and a fine grained paint brush. The specimen should be dried with a cloth towel before applying the next coat of lacquer. The surface of the specimen needs to be carefully and continuously protected when it is not being lapped, as small scratches are difficult to remove during later (fine

grit) stages of the sample preparation. One simple method to protect the specimens is to keep paper towels covering the surface to be analyzed. Another method is to keep the specimen in a plastic baggy.

Paint the sample again with the thinned lacquer, and when dry, mark again with the construction crayon. Lap the specimen with the 100-grit plate until the crayon is removed. Pay close attention and apply even pressure to the specimen as you lap so that one side is not preferentially polished with respect to another. If the crayon is removed evenly from the surface, it only needs to be lapped one time. If not, color the surface again and lap. Recheck the surface with the machinist's rule to ensure the specimen is still flat. Clean the surface of the prepared specimen with fresh water and the fine bristled paint brush. The specimen should be dried with a cloth towel before treated with the lacquer.

Paint the surface again with the thinned lacquer and let it dry. Now lap the specimen on the 180-grit plate. With 180-grit it is difficult to tell when the surface of the specimen is ready to move onto the next plate. The best method is to hold the specimen up to the light at an angle and look for the light to sheen on the surface of the specimen. One should be able to see the sheen of the coarse and fine aggregates. Also one can run his/her thumb over the boundary between the coarse aggregates and the adjacent paste. The specimen should not go to the next stage until this interface feels somewhat smooth. Once a specimen has been deemed finished then it should again be checked with the rule to make sure it is flat. It is very important that there is only a very small relief between the coarse aggregate and paste, as the next plate will never be able to improve the specimen, if the relief depth is large. Once the amount of lapping time is determined on this plate for a specimen with a given aggregate and w/cm then this can be used as a standard minimum amount of time the specimen is lapped before being checked. Clean the surface of the prepared specimen with fresh water and the fine bristled paint brush. The specimen should be dried with a cloth towel before being treated with the lacquer.

Paint the surface again with the thinned lacquer and let it dry before lapping the specimen on the 260 plate. Again, with this fine grit it is very difficult to tell when the sample has received enough lapping, but expect that it will take a significant amount of time to prepare a sample on this plate. One method for checking is to hold the specimen up to the light, and once it is finished, the entire specimen should show a constant gleen from the reflection. Also, one can take the palm of his/her hand, and rub in a circular pattern on the specimen to feel for any relief between the paste and the aggregate. The specimen should again be checked with the rule.

Once this specimen is believed to be finished, it can be taken to a stereomicroscope for viewing. The paste should be inspected at 20x and 50x magnification. In the completed specimen the paste should look very clean. Next, one of the lights should be adjusted to a very low angle, so that the relief of the surface can be inspected. If shadows are cast by coarse aggregates on the surface of the specimen, then more lapping is needed, as the paste has not been polished adequately. If the sample surface looks to be fairly uniform, one should lightly bounce the light with a finger, while inspecting the interface between the paste and an aggregate particle. If the interface between the aggregate and the paste moves as the light bounces, the sample is not finished yet, since this movement indicates that a low shadow between the aggregate and the paste. If the shadow/interface does not move and the paste looks clean and polished, the sample is finished.

Next the sample is soaked in acetone to remove the thinned lacquer. Gloves should be worn when placing and removing the sample from the acetone. This should be completed in a fume hood or in a well ventilated area.

This sample preparation process was developed to be used with limestone or river gravel aggregates with a strength of 5000 psi and a 0.45 w/cm with air contents from 2%-8%. When samples were investigated that contained air content between 6% and 10% more care had to be taken to insure that the walls of the air voids were not damaged. This

can especially be true if several of these voids are close together. If the concrete is weak or of a very high air content then it has been suggested to take the cut specimen and to cover the surface in paraffin wax in an oven. The wax should melt and penetrate into the voids. Now the specimen can be lapped as above without using the thinned lacquer. Once the lapping is finished then the specimen can be put back into the oven while inverted. The wax will again melt and should leave the specimen. This method was never tried in our facility, but was suggested by Jakobsen (2005) of Concrete Experts International, the distributors of the RapidAir.

It was not necessary to lap the specimens in this study to a size below the 260 plate, as polishing of the coarse aggregate occurred and, the marker would no longer stick to the surface, and the reflection from the observation light provided unwanted artifacts in the analysis. However, this should be investigated further for other materials besides the one used in this study.

B.5 LAPPING CLEAN UP

Cleaning the equipment after each use is critical and should follow the following steps:

- Use water to clean the lapper, polishing plates (both sides), and make sure the tub is draining.
- Use a rag to dry off the lapper plates and the lapper itself.
- Allow the magnetic polishing plates to air dry.
- Remove the steel plate with an Allen wrench.
- Make sure both sides are clean.
- Wipe down the steel plate with WD40.

Always make sure the drain is working properly in the lapper, as contaminated standing water can cause the bearing to go bad. Lube the bearing in two places every

three months with a grease gun. The magnetic polishing plates will last much longer if they are kept clean.

B.6 RAPIDAIR 457 SAMPLE PREPARATION

Now that the sample has been lapped, it is ready to be darkened, so that it can be investigated with the RapidAir 457. The surface should be colored with a black ink that will not smear off of the surfaces of the fine or coarse aggregates once it has dried. This is VERY important as these small aggregates are very difficult to color later in the procedure. It was determined that permanent ROUNDED-TIP Sharpie® markers work best. Although the chisel tips would appear to be much more useful for coloring a large surface, it is the author's experience that the ink in that type will smear. Other brands were not tried. After the surface has been completely covered in one direction then the specimen should be rotated 90^{o} and colored again. The specimen should be left to dry overnight to insure the marker has had adequate time to stain the entire surface. The next step is to cover the sample's surface in barium sulfate. This is a very fine powder that is $<1\mu m$ and very white. Next a solid rubber stopper should be used to force the barium sulfate into the surface. The force on the stopper should be just the weight of your hand going up and coming down. After the powder has been forced into the surface the majority of the remaining powder should be brushed off with one's hand. The palm of the hand can be used to pass over the surface of the specimen allowing the extra powder to fall to the ground. This method uses the moisture from the surface of the palm to remove the powder from the surface but not from the voids. Once this is completed the sample should be black with white only in the voids. While rubbing the specimen, black marker will get on the user's hands and will sometimes get into the voids. This needs to be corrected, or the specimen will not be analyzed correctly. If some of the voids do become stained with the black then the specimen can be lightly slapped with your hand while being slightly inverted. This action will cause the stained powder on the surface of

the voids to be removed while leaving the rest of the void still white. One should wash his/her hands after rubbing each specimen.

Now any voids found inside the aggregate need to be colored. While this is a tedious process, with experience it can be completed fairly quickly. The author has found that it is best to first color in all of the coarse aggregate particles that can be seen with the eye. This can be done in a well-lit room or with the specimen illuminated with the microscope lights. After this color application is completed the specimen should then be investigated under the stereo-microscope, and any small voids should be colored with a fine point permanent marker. Care should be taken to only color in the voids in the aggregates. With time one will quickly be able to distinguish air-entrained voids in the paste from voids in the aggregates. The specimen is now ready to be analyzed.

Appendix C: Summary of Test Results for Fly Ash

	fly ash number	1	2	3	4	5	6	7	8	9	10	11	12	13
Chemical Tests	Silicon Dioxide (SiO_2), %	56.18	30.76	36.36	54.75	34.47	52.07	52.04	63.84	49.07	37.16	33.14	35.67	33.28
	Aluminum Oxide (Al_2O_3), %	20.37	17.75	17.44	19.92	20.35	23.65	23.75	18.10	19.72	20.55	18.12	19.56	18.72
	Iron Oxide (Fe_2O_3), %	6.77	5.98	6.08	8.66	5.65	4.55	4.59	4.10	7.87	6.06	6.65	6.47	6.72
	Sum of SiO_2, Al_2O_3, Fe_2O_3, %	83.32	54.49	59.88	83.33	60.47	80.27	80.38	86.04	76.66	63.77	57.91	61.70	58.72
	Calcium Oxide (CaO), %	9.95	28.98	25.68	9.37	26.50	12.76	12.63	8.12	15.12	24.76	27.49	24.62	27.24
	Magnesium Oxide (MgO), %	2.55	6.55	6.15	2.43	4.70	2.02	2.01	1.91	2.93	4.29	5.45	4.58	5.87
	Sulfur Trioxide (SO_3), %	0.53	3.64	2.03	0.46	1.71	0.78	0.79	0.22	1.06	1.23	2.71	2.56	1.85
	Sodium Oxide (Na_2O), %	0.47	2.15	1.90	0.64	1.76	0.31	0.28	0.47	0.66	1.63	1.91	1.73	1.91
	Potassium Oxide (K_2O), %	1.08	0.30	0.46	1.13	0.46	0.80	0.81	1.17	0.95	0.45	0.30	0.48	0.38
	Total Alkalies (as Na_2O), %	1.18	2.35	2.20	1.38	2.06	0.84	0.81	1.24	1.29	1.93	2.11	2.05	2.16
	Classification (ASTM C 618)	F	C	C	F	C	F	F	F	F	C	C	C	C
Physical Tests	mL AEA/100 kg cm for 6% air in	31	44		83	50	138*	147	42	44*	39	36		
	LOI (ASTM C 311)	0.12	0.35			0.11		0.79			0.07			
	Foam Index (mLAEA /g fly ash)	1	1			1		5			1			
	Surface Area (m^2/g)	0.89	0.95					4.02						

* High dosages of WR required for an acceptable slump. This high dosage of WR could cause a change in the AEA demand of the mixture.

	fly ash number	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Chemical Tests	Silicon Dioxide (SiO_2), %	50.98	49.80	47.18	41.32	38.57	33.35	54.59	55.78	31.55	34.62	48.48	51.04	52.56	38.07
	Aluminum Oxide (Al_2O_3), %	18.84	21.63	22.82	19.25	18.84	18.74	20.88	30.59	17.78	21.16	25.01	20.59	19.82	20.75
	Iron Oxide (Fe_2O_3), %	7.87	5.01	4.62	6.48	6.69	6.69	8.56	5.07	6.81	5.69	3.56	8.23	4.72	5.50
	Sum of SiO_2, Al_2O_3, Fe_2O_3, %	77.69	76.44	74.62	67.05	64.10	58.78	84.03	91.44	56.14	61.47	77.05	79.86	77.10	64.32
	Calcium Oxide (CaO), %	14.39	13.01	14.62	21.58	23.54	27.30	9.02	1.10	30.81	25.35	15.92	12.20	14.35	23.78
	Magnesium Oxide (MgO), %	2.91	3.42	3.51	4.43	4.76	5.83	2.65	0.71	4.20	4.62	2.50	2.99	3.16	4.42
	Sulfur Trioxide (SO_3), %	0.95	0.46	0.66	1.25	1.43	1.85	0.51	0.14	2.28	1.55	0.72	0.73	0.92	1.11
	Sodium Oxide (Na_2O), %	0.57	1.42	1.69	1.43	1.71	1.93	0.56	0.27	1.75	1.74	0.30	0.73	0.73	1.65
	Potassium Oxide (K_2O), %	0.94	1.01	0.78	0.78	0.65	0.38	1.19	2.29	0.45	0.47	0.71	1.10	1.11	0.52
	Total Alkalies (as Na_2O), %	1.19	2.08	2.20	1.94	2.14	2.18	1.34	1.78	2.05	2.05	0.77	1.45	1.46	1.99
	Classification (ASTM C 618)	F	F	F	C	C	C	F	F	C	C	F	F	F	C
Physical Tests	mL AEA/100 kg cm for 6% air in	93	49	52			34	49			32	24	48	64	38
	LOI (ASTM C 311)	0.26									1.12	0.63		0.39	0.13
	Foam Index (mLAEA /g fly ash)	3.3									1	1		2.5	1
	Surface Area (m^2/g)											0.96			

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C 138-01	Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete
C 143-05	Standard Test Method for Slump of Hydraulic-Cement Concrete
C 150-07	Standard Specification for Portland Cement
C 173-07	Standard Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method
C 185-02	Standard Test Method for Air Content of Hydraulic Cement Mortar
C 187-04	Standard Test Method for Normal Consistency of Hydraulic Cement
C 230-03	Standard Specification for Flow Table for Use in Tests of Hydraulic Cement
C 231-04	Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method
C 260-06	Standard Specification for Air-Entraining Admixtures for Concrete
C 305-06	Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency
C 311-05	Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete
C 457-06	Standard Practice for Microscopical Determination of Air-Void Content and Parameters of the Air-Void System in Hardened Concrete
C 494-05	Standard Specification for Chemical Admixtures for Concrete
C 618-05	Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete

C 666-03 Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing

C 672-03 Standard Test Methods for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals

C 778-06 Standard Specification for Standard Sand

C 1017-07 Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete

European Norm

480-11 Admixtures for concrete, mortar and grout - Test methods - Part 11: Determination of air void characteristics in hardened concrete

Texas Department of Transportation

DMS 4610-06 Fly Ash

Vita

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